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**THERMAL STABILITY AND
KINETIC STUDIES OF LMH-1**

**C. B. Roberts
and
E. J. Wilson**

FINAL TECHNICAL SUMMARY REPORT

(1 November 1967 to 31 December 1969)

March 1970

**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
EDWARDS AIR FORCE BASE, CALIFORNIA**

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**(PREPARED UNDER CONTRACT Nr. F04611-68-C-0021 BY
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MIDLAND, MICHIGAN 48667)**

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FINAL TECHNICAL SUMMARY REPORT
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March 1970

THERMAL STABILITY AND KINETIC STUDIES OF LMH-1 (U)

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA 93523
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Midland, Michigan 48640

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UNCLASSIFIEDFOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract FO4611-68-C-0021, AFSC Project 3148, Thermal Stability and Kinetic Studies of Aluminum Hydride. The work was administered under the direction of the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California, with Captain Robert W. Bargmeyer, Captain William H. Anders and Lieutenant David Yardley as Air Force Project Officers.

This is a final report on work performed from 1 November 1967 through 31 December 1969.

Management direction at Dow was under Mr. Kenneth W. Guebert, with the work supervised by Dr. Kenneth O. Groves and Mr. Roger D. Daniels. Dr. Charles B. Roberts and Mr. Edwin J. Wilson were co-principal investigators, with Dr. William L. Allen and Mr. Thomas E. Dergazarian making major contributions.

The assistance of Messrs. Ralph VanWert, Charles Schultz and Keith Roberson in performing many of the experiments is gratefully acknowledged.

Abbreviations used in the text are defined in the Glossary.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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SECTION I

(U) ABSTRACT

(C) The thermal stability of magnesium-doped aluminum hydride can be increased seven- to tenfold by controlled hydrolysis treatments; compatibility with propellant ingredients is also greatly improved. A 5-day n-butylamine (2% H_2O) treatment at $80^{\circ}C$. is recommended for future use. Scanning electron photomicrographs reveal the surface characteristics of aluminum hydride crystals and show a thin coating, probably $Al(OH)_3$, generated by hydrolysis treatments. Metallographic studies show that decomposition occurs throughout the crystal, particularly at discontinuities such as voids, cracks, and grain boundaries. Ion probe mass spectrometry shows a higher lithium content near the surface than in the interior of the crystals. Lithium aluminum hydride was extracted from AlH_3 -1451 and is believed to be responsible for nucleation sites which result in the decomposition of AlH_3 . Pound quantities of stabilized AlH_3 have been successfully used in high energy propellant formulations.

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SECTION II

(U) SUMMARY

(C) Post-treatments, consisting primarily of a combined controlled hydrolysis and heat treatment, have resulted in a seven- to tenfold improvement in the thermal stability of aluminum hydride and an improved compatibility with other high energy propellant ingredients.

(C) Treatment for 5-days in n-butylamine containing 2% water at 80°C. is recommended as the best procedure at the present time for magnesium-doped aluminum hydride. This treatment produces a material with good thermal stability (15-25 days to 0.1% at 60°C.), a low oxygen content (~1%), and it has a proven compatibility with high energy propellant ingredients.

(C) Treatment for 5 days in ethanol containing 2% water at 80°C. produced aluminum hydride with better thermal stability than the NBA method. The best samples required 35-40 days to reach 0.1% decomposition at 60°C. Compatibility with TVOPA is poorer and the increase in oxygen content is greater than for NBA treated samples.

(C) Aluminum hydride hydrolyzes slowly in water buffered at pH 7. After drying, the hydride has an improved thermal stability and excellent compatibility with TVOPA and TEGDN. For a given amount of hydrolysis (measured by oxygen uptake during treatment) the increase in thermal stability is poorer than the NBA or EtOH treatments at 60° or 80°C.

(C) Aluminum hydride treated 3 days in a pH 7 solution and followed by a 5-day treatment in ethyl alcohol containing 2% water at 80°C. has a thermal stability comparable to the NBA-treated material. It has better compatibility with TVOPA than the latter, but oxygen uptake during the treatment is almost double (2% vs. 1%). Aluminum hydride treated by this method is being evaluated in high energy propellant formulations.

(C) Aluminum hydride treated 3 days in a pH 7 solution, followed by a 5-day treatment in bis(2-methoxy)diethyl ether (diglyme) containing 2% D₂O at 80°C., produced two hydride samples which required 34 and 39 days to reach 0.1% decomposition at 60°C. The oxygen contents were 2.6% and 2.1%, respectively.

(C) The water which is in the solvents used for treatments is necessary for an improvement in thermal stability. Treatments in solvents with low water contents (<0.1%) resulted in a loss of stability or an exothermic reaction of the hydride with the organic solvent.

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(U) The ion probe mass spectrometer revealed a higher lithium content near the surface of the crystals than in the interior. Metallographic studies showed that metal nucleation begins at crystal discontinuities, such as cracks, voids, and grain boundaries.

(C) The scanning electron microscope was used to examine crystal surfaces. These studies showed that less stable samples are characterized by small agglomerated crystals, that microscopic material adheres to the surface of some crystals, and that a surface coating is generated on the hydride crystals during stabilization treatments.

(C) Lithium aluminum hydride was extracted with diethyl ether from finely ground aluminum hydride containing 0.40% lithium. However, only one-quarter of the lithium could be removed by this technique.

(C) The lithium content of aluminum hydride was shown by a computer analysis of data from several hundred lots of pilot plant hydride (Texas) to be the most important factor in thermal decomposition. The correlation between lithium content and stability is inverse, i.e. the lower the lithium content the better the stability.

(C) Lithium aluminum hydride is the most important impurity since it probably initiates decomposition and is also a major cause of compatibility problems. Deactivating the lithium aluminum hydride by a combination hydrolysis - heat treatment (NBA) results in greatly improved thermal stability and compatibility.

(C) The surface coatings of stabilized hydride could not be identified directly by electron diffraction. Density measurements and elemental analysis of highly hydrolyzed samples lead to the conclusion that the coating is amorphous aluminum hydroxide. It improves the compatibility of the hydride with other propellant ingredients by preventing active species such as water or hydrogen fluoride from penetrating the crystal.

(U) Purifying the starting materials and solvents and carrying out the synthesis in a dry box did not result in either improved crystallinity or thermal stability.

(U) Drying procedures for stabilized material were improved; this reduced "initial gassing" to below 0.01%.

(C) Exploratory research was done on an alternate method of stabilizing AlH_3 -1451. This method, a heat treatment with diphenylacetylene at 160°C., resulted in partial decomposition with the formation of 5-15% aluminum, but it has an advantage of increasing stability without adding oxygen.

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(U) Good agreement was found between stability as measured by weight loss on a Cahn electrobalance and pressure increase (transducer).

(C) Pound quantities of both magnesium-doped hydride and non-doped hydride were prepared by three different stabilization techniques for propellant evaluation. Although evaluation by the Lockheed Propulsion Company is incomplete, the stabilized lots which showed the best neat thermal stability produced the most stable propellant.

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SECTION III

(U) TECHNICAL RESULTS AND DISCUSSION

(U) Improvements in the thermal stability and compatibility of aluminum hydride (AlH_3 -1451) in propellant ingredients were accomplished by:

- (1) Using the best analytical techniques to determine the mechanism by which decomposition is initiated and propagated, and
- (11) Applying this knowledge to increase the effectiveness of stabilization techniques.

(U) With few exceptions, the aluminum hydride used for experimental purposes and referred to in this report was comprised of pilot plant lots made by the batch process in Freeport, Texas. These lots vary widely in thermal stability, chemical reactivity with water, crystalline perfection, and purity.

(C) As a result of the research described in this section, the following was accomplished:

- (1) Techniques to characterize aluminum hydride thoroughly prior to its use in a propellant formulation were established.
- (11) Post-treatments which greatly improve the quality of aluminum hydride for propellant applications were developed; the most effective treatment is recommended for future use.
- (111) The thermal stability of neat aluminum hydride and aluminum hydride-plasticizer mixtures was measured with a high degree of accuracy in the 0-0.1% decomposition range.

A. ANALYTICAL STUDIES (U)

(U) In the first phase of the program all instrumental analytical techniques which were potentially useful in analyzing aluminum hydride, its impurities, and/or products of reaction or decomposition were considered. The purpose of this part of the program was to determine which methods could reliably detect differences between samples with widely varying stabilities, and to characterize species involved in the decomposition process(es).

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It was recognized that some of the methods would be of no value, some would be of marginal utility, and a few would provide valuable information. After the screening program was completed, only those methods which demonstrated utility were used. A discussion of each method and the experimental results obtained from its application are presented.

1. Surface Characterization (U)

(C) The chemical composition and physical properties of the surfaces of aluminum hydride crystals have been of prime interest since it was previously discovered that thermal decomposition and chemical reactivity are initiated primarily at these surfaces, both internal and external (1). It is extremely difficult to obtain an elemental analysis of internal surfaces (cracks, fissures, grain boundaries, etc.). The external surfaces are more amenable to analysis; for example, the topographical features of the crystals can be determined by the scanning electron microscope which has a useful magnification up to approximately 20,000X. In addition, an ion probe mass spectrometer can be used to determine the concentrations of lithium, magnesium and oxygen on the external surfaces. While there is risk in assuming that internal surfaces behave chemically the same as external surfaces, metallographic studies indicate that the formation and growth of aluminum nuclei are very similar for both (Section D.1). Therefore, the external surfaces of the cubic crystals found regularly in the pilot plant material and surfaces which result from discontinuities in the interior of the crystal may respond to stabilization treatments in essentially the same manner.

a. Elemental Analysis by the GCA* Ion Microprobe Mass Spectrometer (U)

(U) The ion microprobe mass spectrometer is used to analyze solids; it consists of a primary ion source to produce secondary ions from a test specimen by ion sputtering and a mass analyzer assembly to characterize the secondary ion beam. The ion source generates a very dense argon plasma which is focused onto the sample; the interaction of the ion beam and the sample (referred to as sputtering) produces atomic and molecular fragments, some of which are charged. The positive ions are then focused into a mass spectrometer for qualitative and quantitative analyses. The depth to which the ion beam penetrates the solid sample is controlled by changing the intensity of the argon plasma beam.

(C) The first samples selected for analysis by the IMS-101B provided a wide range of bulk lithium concentrations (0.12 to

* Geophysical Corporation of America, Bedford, Massachusetts.
Analyses performed by Dr. F. G. Satkiewicz of GCA.

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0.25%) and a correspondingly wide range in thermal stability (34 to 7 days to 1% decomposition at 60°C.). Those studied were:

- (i) Lot 08187 - "as received", DPA treated, 34 days to 1% decomposition at 60°C., $L_i = 0.12\%$.
- (ii) Blend 39-16-1 - n-butylamine treated 33 days to 1% decomposition at 60°C. (prior to treatment, the stability was 13 days), $L_i = 0.17\%$.
- (iii) Lot 05316 - "off grade", 7 days to 1% decomposition at 60°C., $L_i = 0.25\%$.

(C) Results of these analyses (Figure 1) revealed a lithium gradient within the first micron of the crystal. Lot 05316, a poor stability sample, had a high lithium content near the surface, whereas Lot 08187, a good stability sample, had a lower lithium concentration near the surface as well as in the interior of the crystal. The n-butylamine treated blend (39-16-1) had a higher lithium content at the surface, but this decreased rapidly.

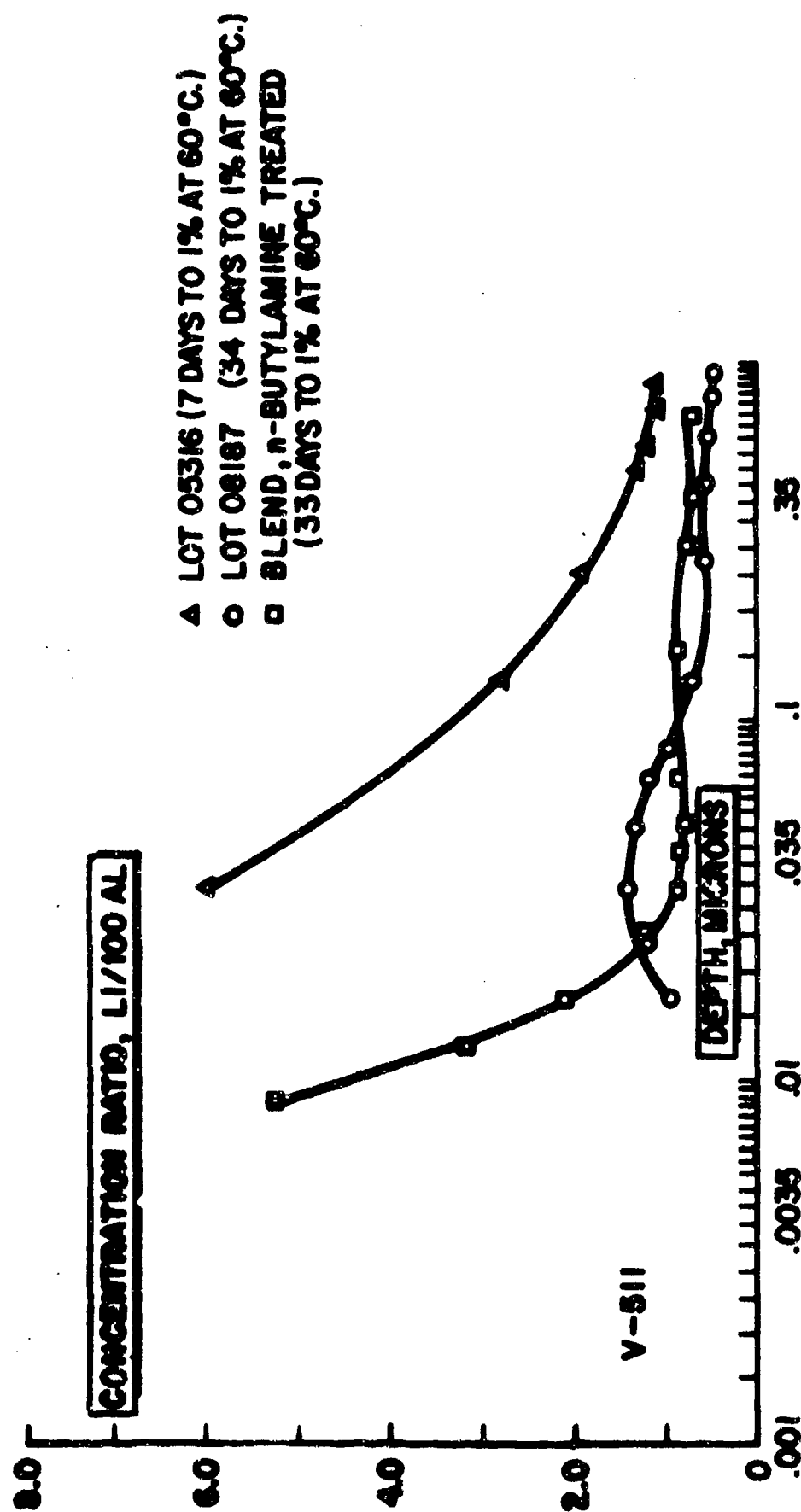
(C) The second set of samples analyzed by the IMS were from the same Texas pilot plant lot, 11177. The lithium, magnesium, and oxygen profiles were obtained for the material (i) "as received," (ii) NBA-treated 18 days at 60°C., and (iii) pH 7 hydrolyzed 10 days. The purpose of these experiments was to determine changes in concentration of these three elements which resulted from the treatments. All three treatments increased the thermal stability from 27 days to 1% decomposition at 60°C. to 50-60 days to 1% at the same temperature.

(C) The lithium profiles (Figure 2) show a reduction of surface lithium as a result of the hydrolysis treatments. Lithium concentrations at 1μ are in agreement with the bulk value of 0.007 atomic fraction (L_i/A_i) determined by elemental analysis (0.15 wt. % lithium).

(U) The results from the limited number of experiments for magnesium and oxygen are difficult to interpret and correlations with stability are inconclusive.

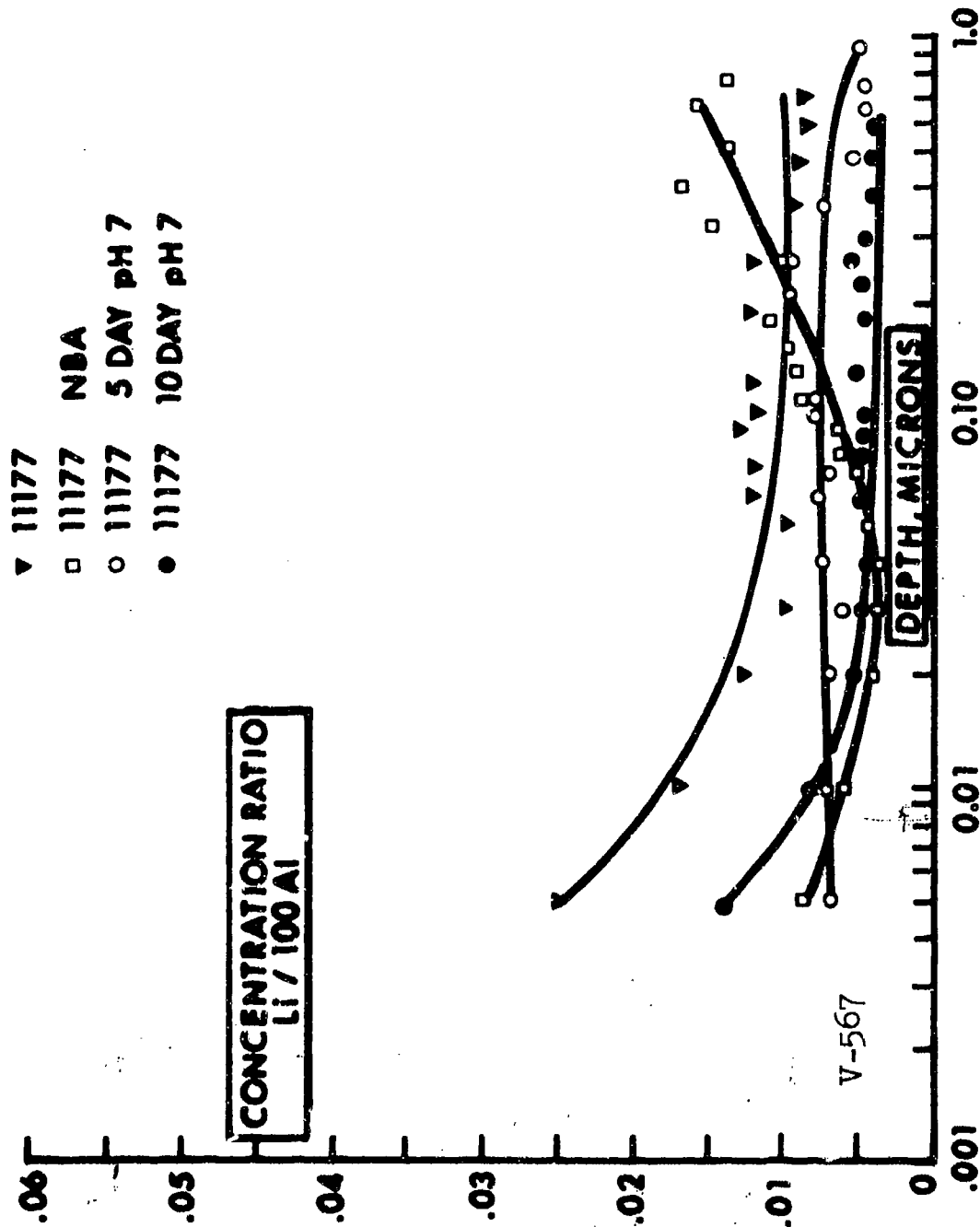
(C) The magnesium profiles of these samples (Figure 3) show that the hydrolysis treatments tend to increase the amount of magnesium on the surface; the longer hydrolysis time (10 days) accentuates this effect. The constant concentration reached at about 0.1μ is equivalent to the bulk magnesium concentration (1.4-1.5 wt. % magnesium).

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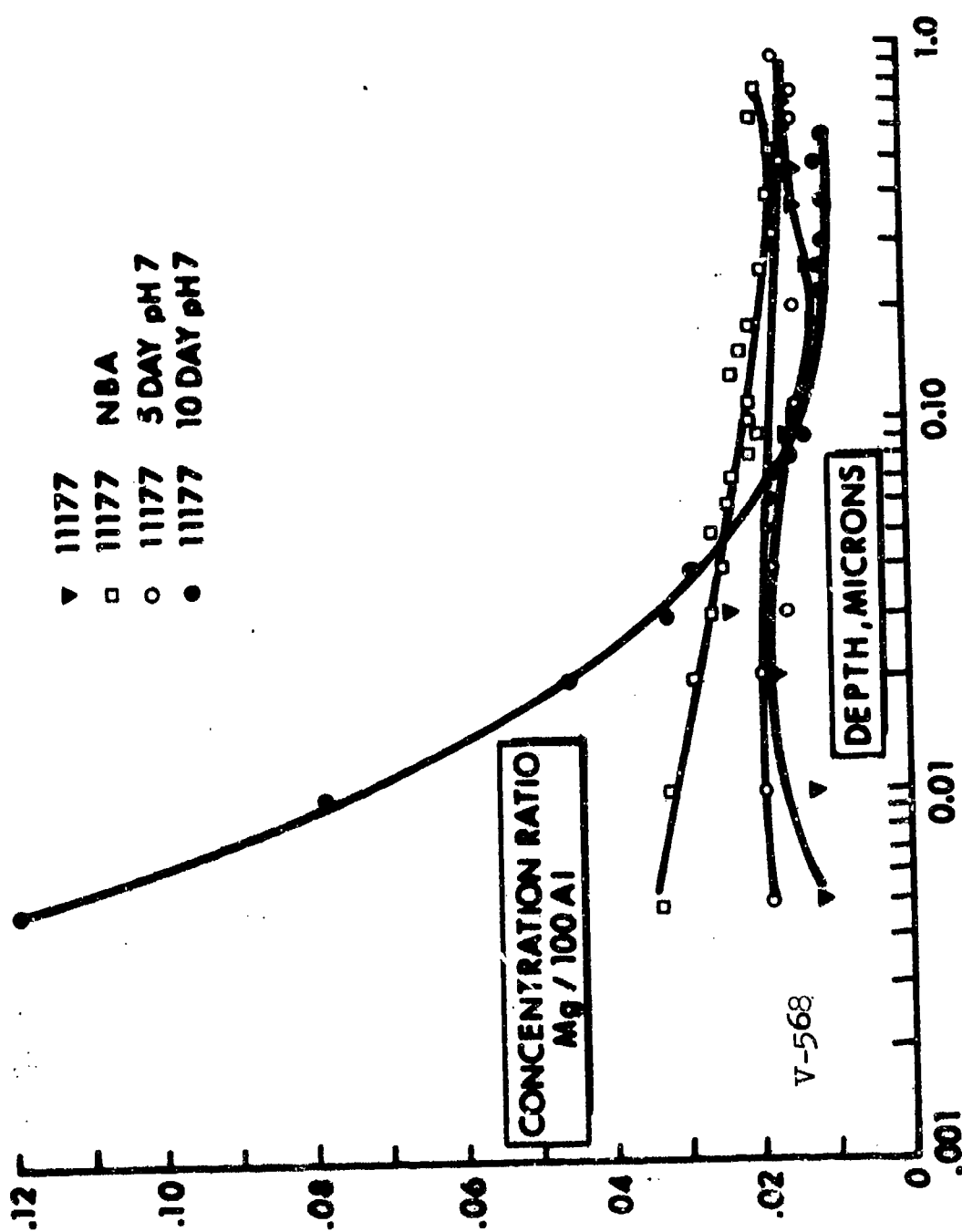
(U) Fig. 1 - Lithium Profiles at Surface of AlH₃-1451

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(U) Fig. 2 - Lithium Profile Analysis of Lot 11177B

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(U) Fig. 3 - Magnesium Profile Analysis of Lot 11177B

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(C) The oxygen profiles (Figure 4) show a significant difference between the pH 7 hydrolyzed and NBA hydrolyzed samples. The pH 7 treated samples had a maximum oxygen content at the surface; it decayed to the bulk concentration at about 0.5μ . The NBA hydrolyzed sample had an oxygen-rich zone centered at 0.05μ . The difference may be due to diffusion of the oxygen (or water) into the crystal as a result of the heat treatment associated with the NBA method. The ordinate axis in Figure 4 shows the oxygen-aluminum ion current ratio, but no correction was made for the sputtering efficiency of oxygen. Hence, the values indicated on the graph show only comparative values for oxygen.

(C) Prior to this investigation, it was believed that the differences in concentration of lithium, oxygen, and perhaps magnesium between the surface and the bulk would be large ($>10X$) and that treatments would produce changes which would correlate with improvements in stability. While these changes were not as large as expected, differences were found. The lithium profiles are particularly noteworthy since they consistently show the more stable samples, both treated and "as received," to have low concentrations of lithium at the surface. This agrees with other data (see Section D.3.b.) which show a similar relationship between lithium content and stability.

b. Surface Examination by Scanning Electron Microscope and Electron Diffraction (U)

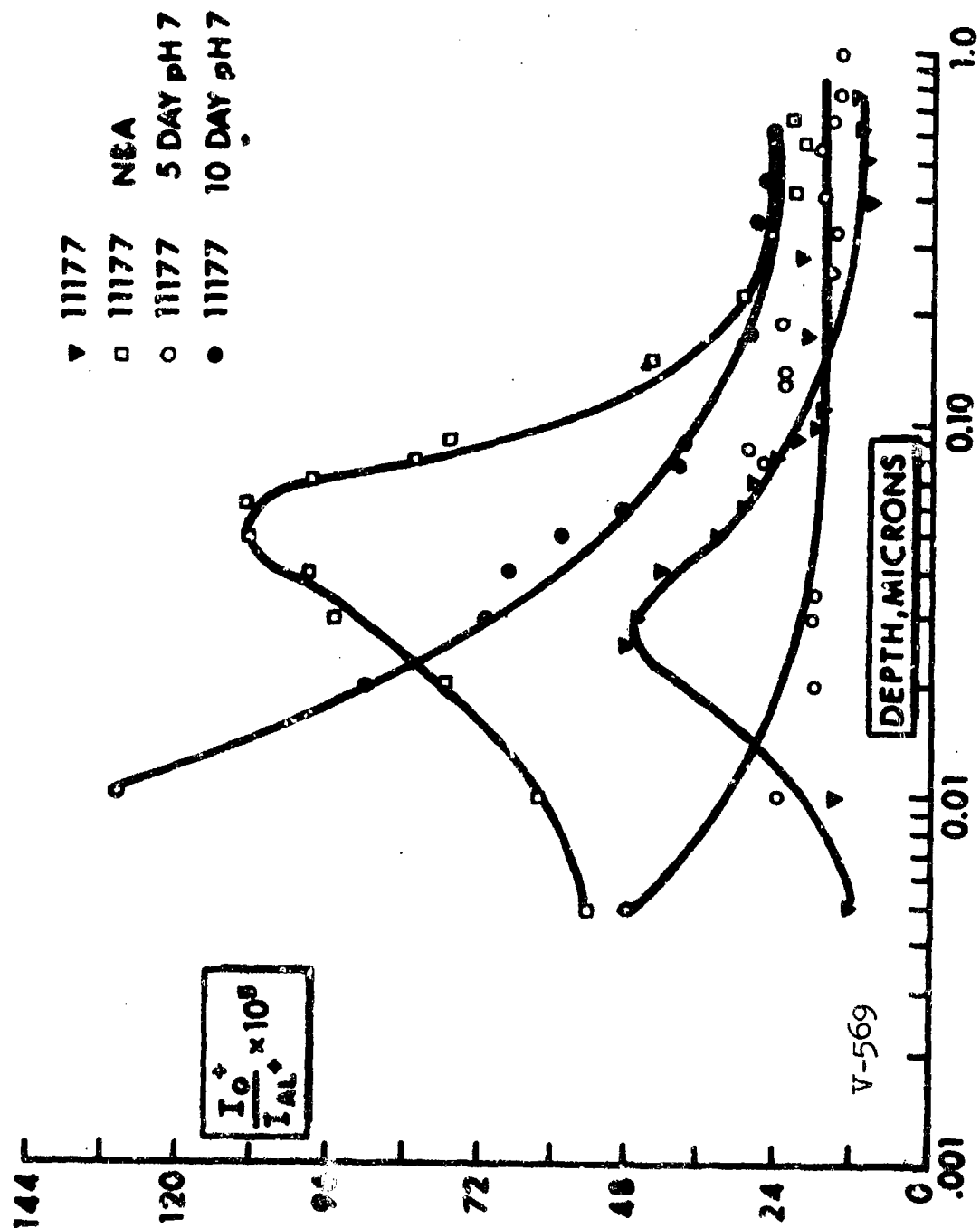
(U) The scanning electron microscope uses a 10-30KV electron beam, focused by three magnetic lenses, to excite the surface of a target material. The secondary electrons (~ 50 volts in energy) emitted from the target are collected and amplified by a photomultiplier. The intensity of the secondary electron emission depends primarily upon the distance of the target area from the collector. Scanning the electron beam across the surface of the target material and displaying the output on the screen of a cathode ray tube gives a micro-topographical picture of the surface.

(U) Scanning electron photomicrographs of various lots of aluminum hydride show differences in crystal perfection, size, and surface appearance*. Several of these microphotographs are shown in Figures 5-11.

(C) The information obtained from these photomicrographs is qualitative, but it is useful in conjunction with data from other areas of investigation such as the metallographic studies. Trends which emerged from the examination of these photomicrographs are listed below:

*SEM pictures obtained with the help of Everett Sutton and Harry Baker of the Microscopy Laboratory of The Dow Chemical Company.

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(U) Fig. 4 - Oxygen Profile Analysis Lot 11177B

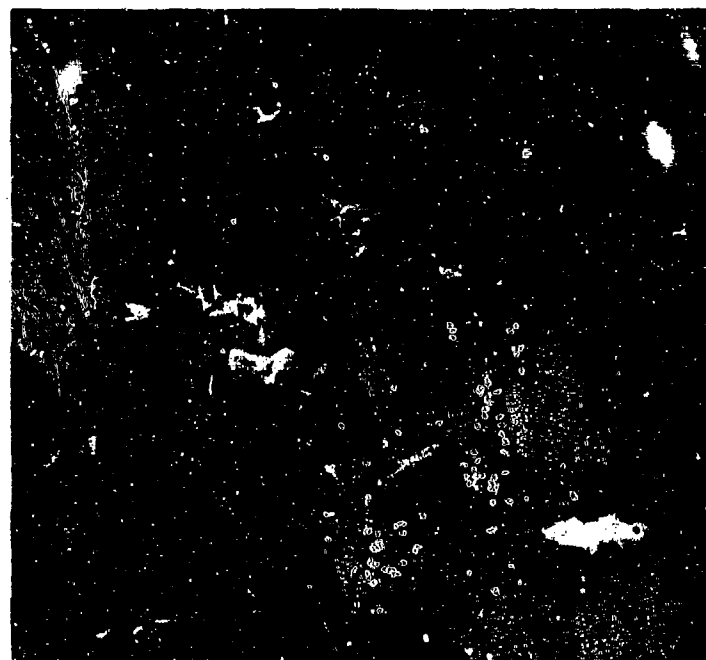
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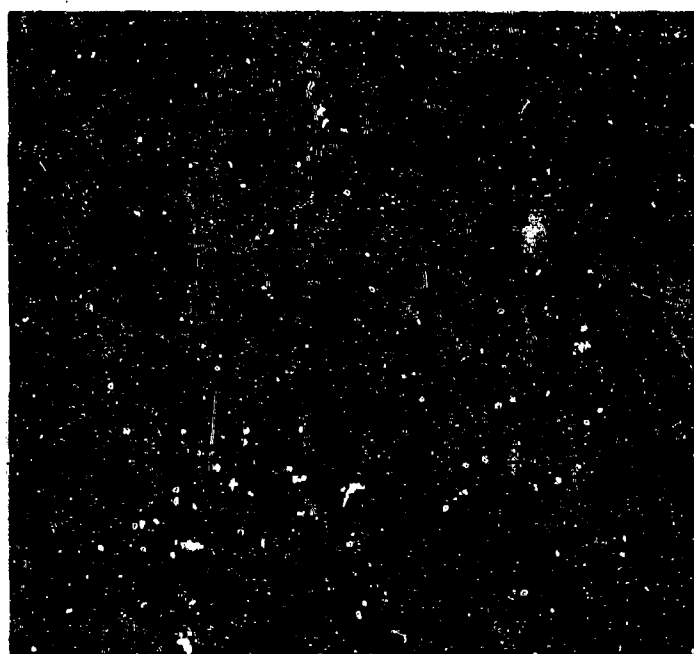
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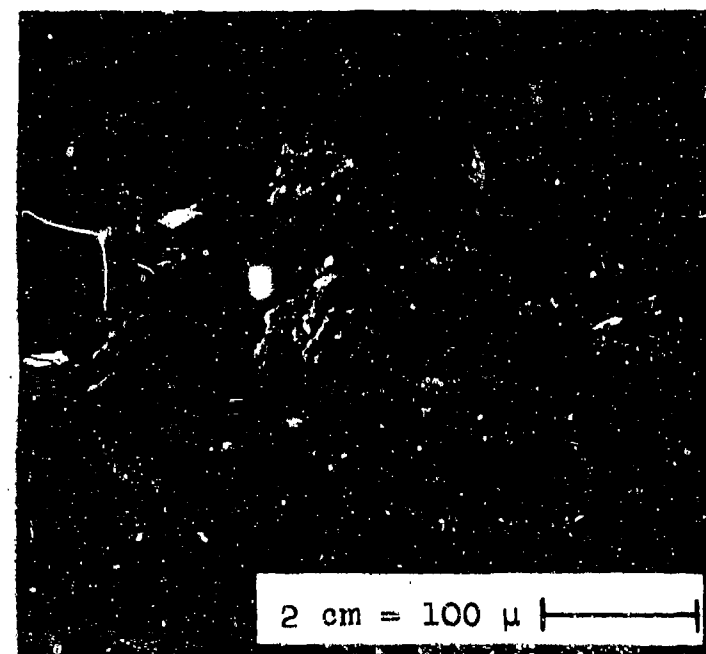
A. Lot 07155



B. Lot 08176



C. Lot 05316



D. Mini-plant Product

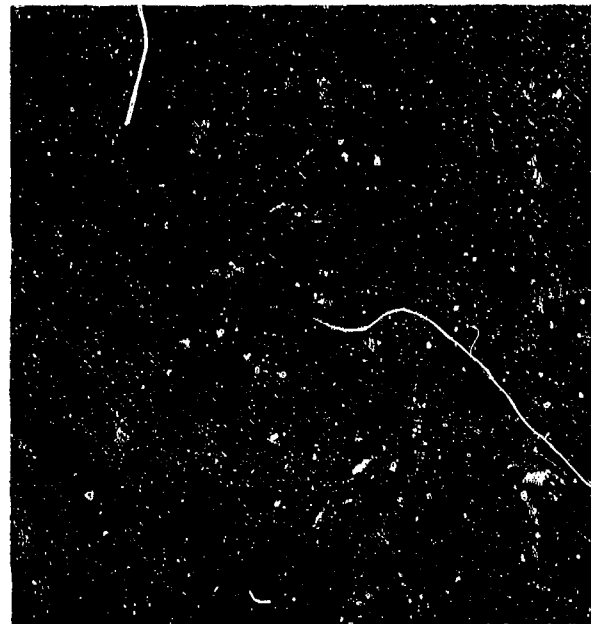
(U) Fig. 5 - Off-Specification "As Received"
AlH₃-1451 at Low Magnification (X200)

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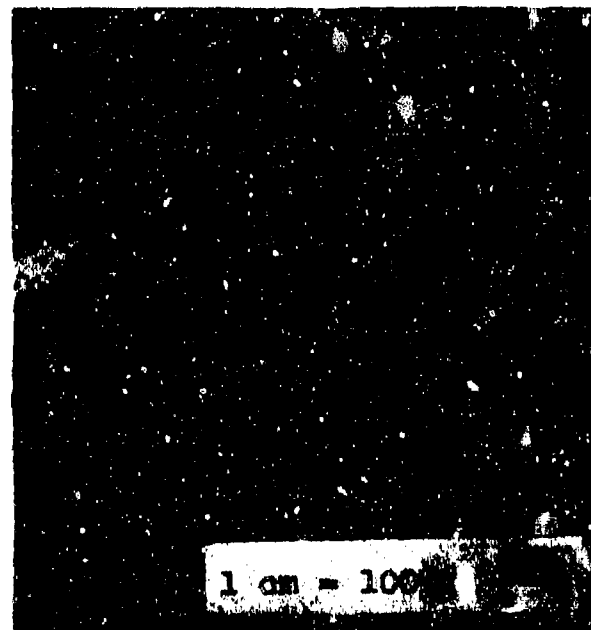
A. Lot 02038



B. Lot 10107



C. Lot 08187



D. Lot 11217

(U) Fig. 6 - Stable "As Received" AlH_3 -1451
at Low Magnification (X100)

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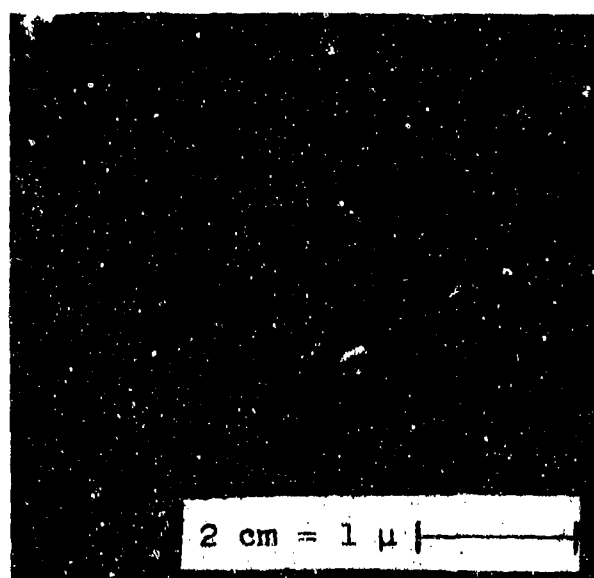
A. Lot 08176



B. Lot 02038



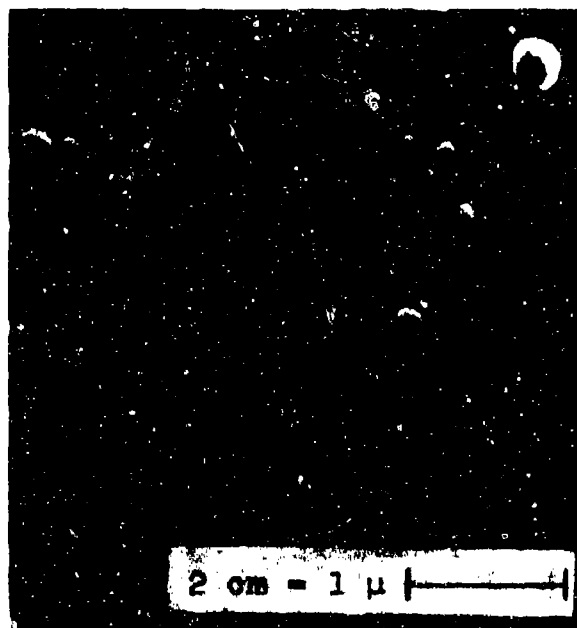
C. Lot 08187



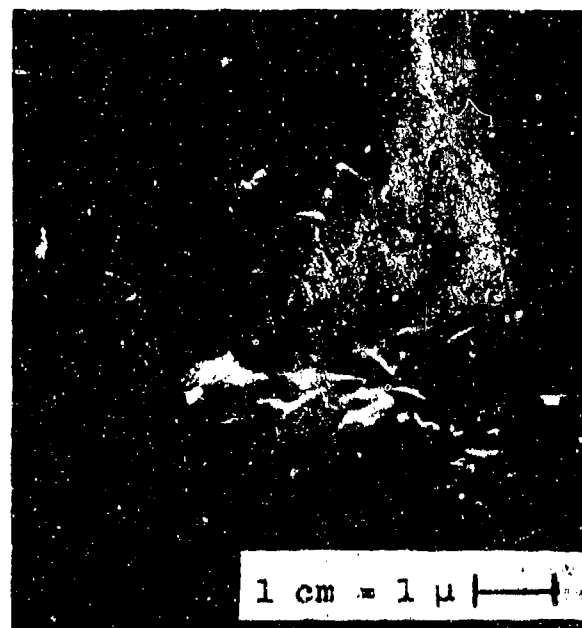
D. Lot 11217

(U) Fig. 7 - "As Received" AlH₃-1451 Surface
at High Magnification (X20,000)

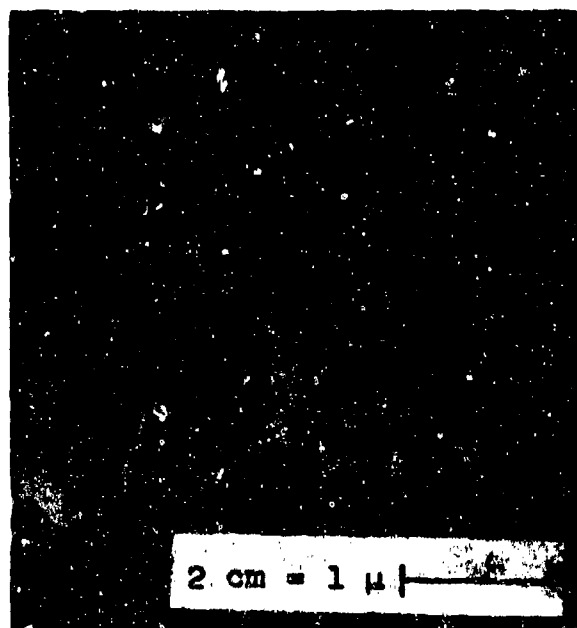
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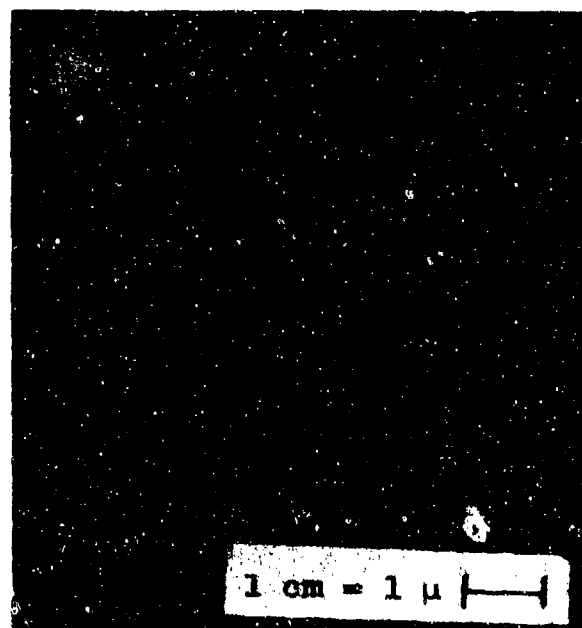
A. 7% (X20,000)



B. 14% (X10,000)



C. 7% (X20,000)



D. 17% (X10,000)

(U) Fig. 8 - Partially Decomposed Aluminum Hydride

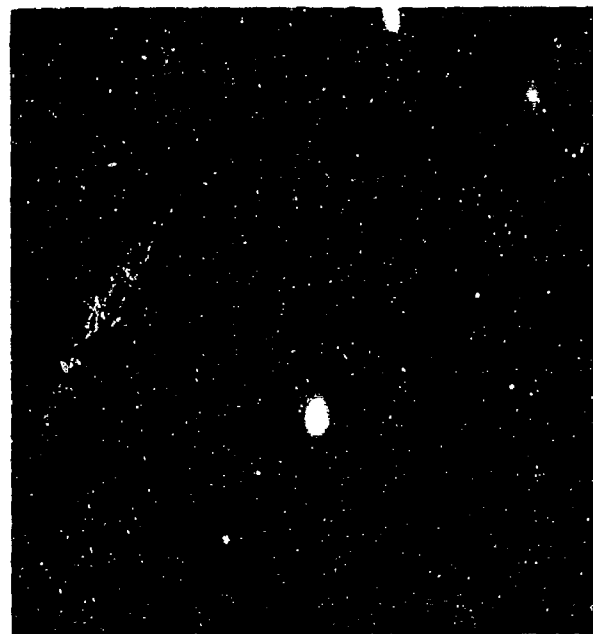
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A. Lot 11217 n-Butylamine
Treated



B. Lot 05316 n-Butylamine
Treated at 60°C.



C. Lot 05316 pH 7 Hydrolyzed
9 Days



D. 12-Lot Blend n-Butylamine
Treated for Contract
AF 04(611)-11606

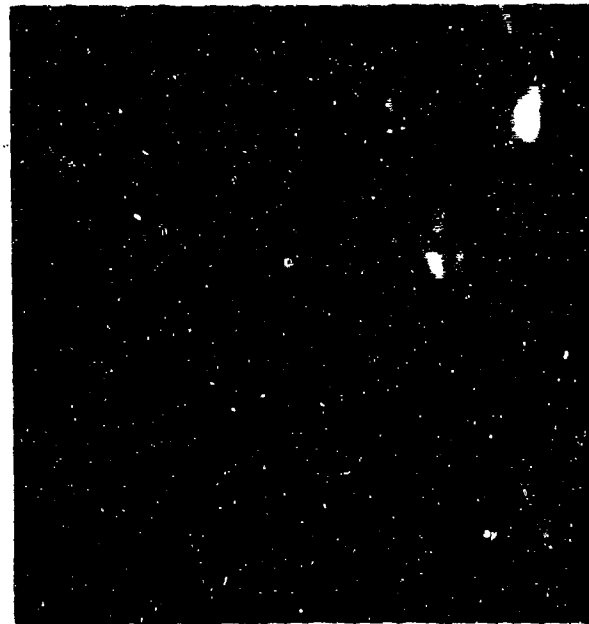
(U) Fig. 9 - AlH₃-1451 Surface Coatings Resulting
from Hydrolysis Treatments (X20,000)

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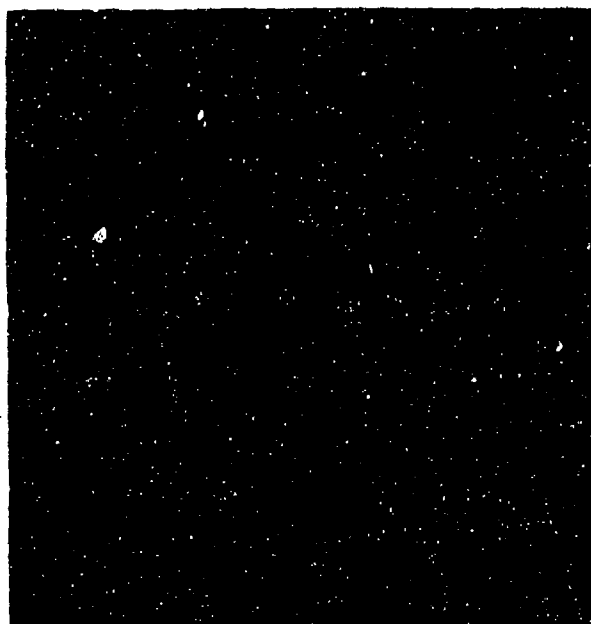
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A. Lot 02038



B. Lot 10107



C. Lot 08187



D. Lot 11217

(U) Fig. 10 - "As Received" AlH_3 -1451 Surface
at Intermediate Magnification (X2,000)

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- (1) Less stable samples are characterized by small, agglomerated crystals (Figure 5). More stable samples tend to be large, "single" crystals (Figure 6). Holes in the crystals, e.g. Lot 11217, do not impart poor thermal stability to the material.
- (ii) Microscopic-sized material adheres to the surface of the crystals, and varies in amount from lot to lot (compare Lots 02038 and 08187 in Figure 7). Because of the minute quantities involved, it has not been possible to identify this material. However, hydrolysis treatments do not remove it, and as far as can be determined, it is inert. Partially decomposed samples show a uniform pattern of decomposition (dark areas) independent of the distribution of adhering particles (Figures 8 A,C,D).
- (iii) A surface coating is generated on the hydride crystals as a result of pH 7 and n-butylamine treatments (Figure 9). Coating thickness depends on the type of treatment, length of treatment, water content in the organic solvent, and original stability of the material. The texture of the coating also varies, even for the same stabilization treatment (Figures 9 A,B,D).
- (iv) Highly magnified surfaces indicate that crystal growth is accomplished by the building up of layers which overlap each other (Figure 10). If this is the growth mechanism, numerous discontinuities must exist throughout the crystal.
- (v) Well formed symmetrical platelets appear on the surfaces (Figure 8 B) of some samples, particularly following an acrylonitrile (AN) treatment. An attempt was made to identify both the platelets, which appeared to be crystalline, and the surface composition of treated and untreated aluminum hydride by electron diffraction. The initial experiments were performed by transmitting a 100 KV beam through thin specimens which had been fractured from the surfaces of the hydride samples. The diffraction patterns showed only AlH_3 -1451 and aluminum (due to decomposition by the 100 KV beam). No diffraction patterns were obtained from the coatings of the pH 7 and NBA treated samples.

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(C) A sample of AN treated material which was covered with platelets was analyzed by reflectance electron diffraction, but no phase or crystalline compound other than AlH_3 -1451 was found. Possible reasons for this are:

- (i) The platelets are in such small quantities compared to the bulk of the material that diffraction techniques lack the sensitivity to identify such a weak pattern.
- (ii) Although the platelets appear to be crystalline in the photomicrographs, they may be amorphous. If this is the case, characterization by diffraction techniques is impossible.
- (iii) The platelets may be AlH_3 -1451 crystals and cannot be distinguished from the bulk diffraction pattern of the bulk AlH_3 .

c. Metallographic Studies (U)

(U) The utility of the metallograph technique for detecting the formation of aluminum nuclei has been previously demonstrated (1). Although this method was improved to detect the early formation and growth of aluminum nuclei (1% decomposition), its development under this contract was of less importance than its application. This latter aspect is discussed in detail in Section III.D.1.

d. Other Analytical Methods for Surface Analysis (U)

(U) Laser emission spectroscopy was considered as a back-up for the ion probe mass spectrometer. However, it was shown to be impractical since the minimum energy of the laser beam would vaporize an entire 100 μ crystal.

(U) Raman laser and infrared spectrometry are excellent methods for identifying adsorbed or chemiadsorbed species on the surfaces of solids; neither proved useful in this work. Raman laser spectroscopy showed no absorption for the NBA hydrolyzed samples, but did show a peak at 710 cm^{-1} for pH 7 hydrolyzed samples. This peak was believed to result from Al-O bonding. Infrared spectroscopy detected only the Al-H absorption peaks which were the same for all samples.

(U) Surface area measurements by a conventional volumetric BET apparatus using nitrogen gas revealed that the specific area for representative samples was less than the minimum sensitivity of the technique ($1.0 \text{ m}^2/\text{g}.$). Lockheed Propulsion Company (2) reported the specific area of two pilot plant lots (Texas) to be in the order of $0.1 \text{ m}^2/\text{g}.$

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(U) Later work with a one-point modified BET system showed some correlation of surface area with stability. However, the precision of the method was poor: therefore, the reliability of the results was doubtful. No further work was done in this area since meaningful results would have required either purchasing or assembling the necessary equipment, and this was not considered essential at the time.

2. Analysis of Off-Gases by Mass Spectrometer and Weight Loss Measurements (U)

(U) Previous mass spectrometric analyses of the off-gases resulting from aluminum hydride decomposition have shown that numerous gases are evolved, particularly in the first 0.2% decomposition (3). The origin and possible effect of these gases or their precursors on the decomposition process were unknown, although it was believed that their presence was due to impurities in the hydride lattice. Since these results were inconclusive, a more thorough effort was made to correlate the gaseous decomposition products of AlH_3 -1451 to the initiation and propagation of AlH_3 -1451 decomposition.

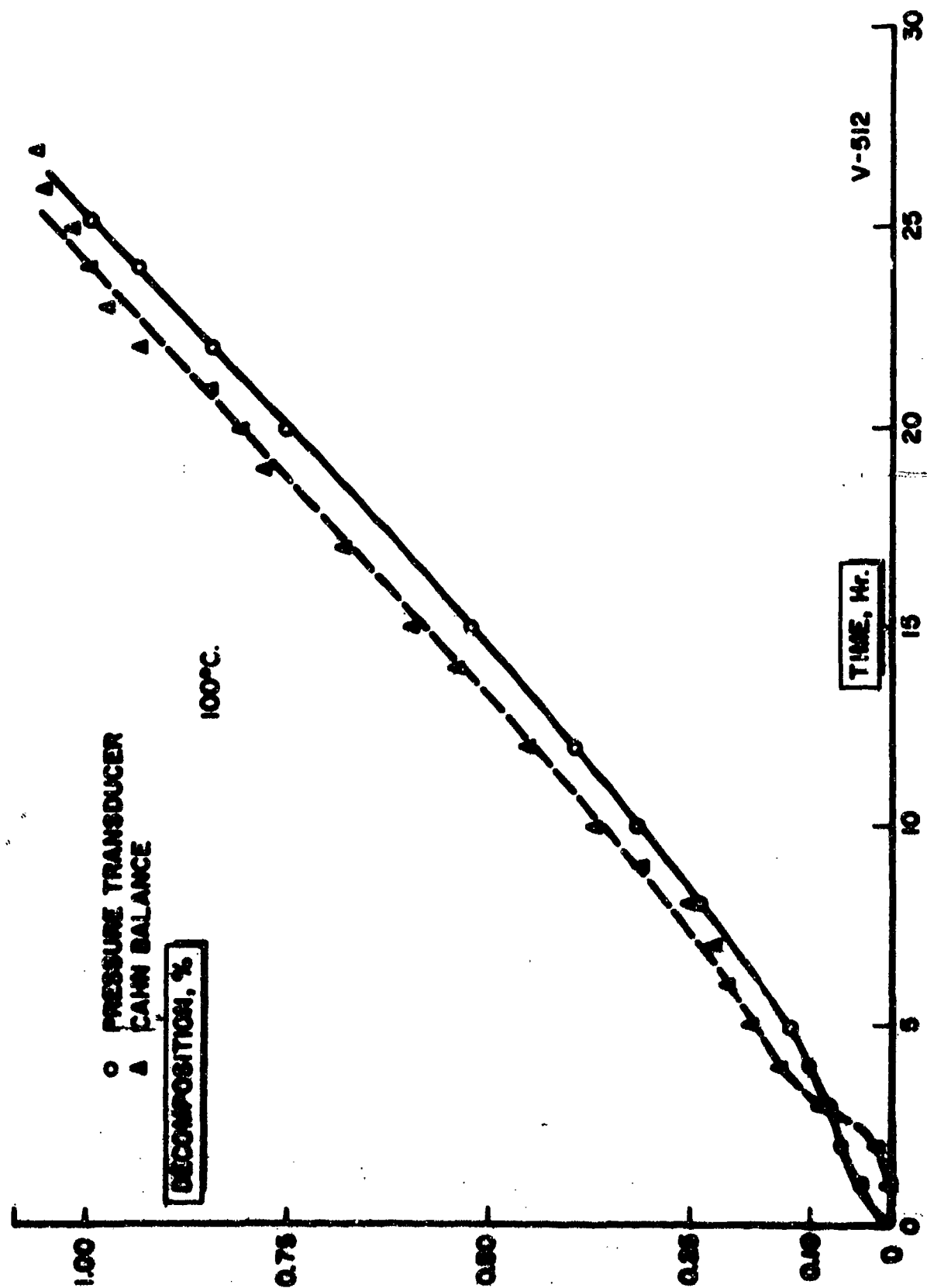
(U) A combination mass spectrometer-Cahn vacuum electrobalance was used to monitor the off-gases and simultaneously record the weight loss (amount of decomposition). The analysis of samples of widely varying stabilities showed only the presence of hydrogen, water, benzene and diethyl ether, all of which are present in the manufacturing process. It was concluded that the other gases found in previous work were not associated with decomposition and that the analysis of off-gases could not provide an insight into the mechanism of aluminum hydride decomposition.

(U) This technique, however, did reveal that all samples treated by a hydrolytic method underwent a comparatively large weight loss following evacuation of the system at room temperature (Table I). Analysis of these off-gases by mass spectrometry showed that the weight loss was due mainly to the desorption of water. This water could be removed by either evacuation for 16 hrs. at ambient temperature or one hour at 100°C . These data were the first indication that water from an incompletely dried sample is a major component in the initial off-gases and suggested the investigation of drying techniques reported in Section III.C.2.

(U) Weight losses, as measured by the Cahn balance, were used as an independent check on the pressure transducer for measuring decomposition. Figure 11 shows the decomposition curves at 100°C . of each method for Lot 11217, NBA treated. The irregularity at the beginning of the curves is due to slightly different drying procedures.

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(U) FIG. 11 - Comparison of $\text{AlH}_3\text{-1451}$ Decomposition Rates by Cahn Balance and Pressure Transducer

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Table I

(U) Weight Loss Behavior of 18-Day
n-Butylamine Treated AlH₃-1451

<u>Time</u> <u>hr.</u>	<u>Wt., mg.</u>	<u>Wt. Loss</u> <u>mg.</u>	<u>Pressure</u>	<u>Apparent</u> <u>Water Loss</u> <u>%</u>	<u>Temp.</u>
0	451.23	--	Atm.	--	Ambient
0.17	450.78	0.45	Continuous evacuation	1.0	Ambient
2.8	450.40	0.83	Continuous evacuation	1.83	Ambient
3.5	450.40	0.83	~10 μ	1.83	Ambient
8.3	449.72	1.51	~5 μ	3.34	100°C.

3. Application of Other Analytical Methods (U)

(U) The conventional elemental analysis methods continued to be used and a method for predicting the thermal stability of aluminum hydride by DTA was investigated. Mass thermal analysis (MTA) and wide line proton nuclear magnetic resonance (NMR) did not yield useful information.

a. Differential Thermal Analysis (DTA) (U)

(U) The reaction kinetics of AlH₃-1451 decomposition was studied by DTA. The most useful data were obtained at temperatures in the region of the maximum endotherm; information obtained on activation energies and position of the endotherm vs. stability agreed with previously published data (4). Extrapolation of these data to predict accurately the time required for a sample to reach a low degree of decomposition, e.g. 0.1% or 1.0%, was very difficult, particularly since operating techniques affect the temperature at which the maximum endotherm occurs. For example, samples of Lots 05316 (7 days to reach 1% decomposition at 60°C.) and 11217 (32 days to 1% decomposition at 60°C.) were compared using a slow heating rate (5°C./min.) and a fast heating rate (15°C./min.) while maintaining all other instrumental conditions the same. The DTA curves at the slow heating rate showed that the maximum endotherm for Lot 11217 occurred at a temperature five degrees higher than for Lot 05316. At the faster heating rate, the difference in temperature between the maximum endotherms of the two samples was considerably less than 5 degrees. Since this quite small temperature differential represents 25 days of stability at 60°C. (the difference in thermal stability between the two samples), it is apparent that changing the heating rate significantly affects the predicted stability of the samples. These results

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showed that the DTA method can be used as a stability screening technique, but that exact stability data must be obtained by more reliable methods such as the pressure transducer or Taliani apparatus.

b. Mass Thermal Analysis (MTA) (U)

(U) The mass thermal analysis method involved coupling a differential thermal analysis (DTA) apparatus to a Bendix time-of-flight mass spectrometer. Thus, thermal changes observed by DTA can be related to a specific reaction by identifying the gaseous products of decomposition. The sensitivity of the DTA instrument was too low to detect thermal changes at temperatures below 160°C., and, consequently, correlations of gaseous products with low temperature thermal changes could not be made. Since more meaningful data could be obtained by the mass spectrometer or DTA alone, experimental work with the MTA technique was discontinued.

c. Wide-Line Proton Nuclear Magnetic Resonance (NMR) (U)

(U) Four AlH₃-1451 samples were examined by wide-line proton NMR. These samples included off-grade, pH 7 hydrolyzed, NBA treated, and stable (untreated) materials. Two components, a broad line and a narrow line, were seen in the NMR spectra. The broad line signal results from the major component, solid AlH₃. Its width is about 17 gauss and its shape was identical for all four samples. The narrow line is due to protons possessing relatively high mobility, presumably an occluded organic phase or adsorbed water. The narrow line was only slightly higher for the pH 7 and NBA treated samples than for the untreated samples, and reflects residual n-butylamine and/or water from the treatment. No further work was done using wide-line NMR.

d. Elemental Analysis (U)

(U) The purity of numerous samples both prior to and after stabilization treatments was determined. These data for the five Texas pilot plant lots which were most thoroughly studied are listed in Appendix A. The purity of the sample and its relationship to thermal stability are important; consequently, stability data are presented for each sample.

(C) Oxygen was incorporated in varying amounts during the stabilization treatments; the concentration was determined by activation analysis. All other elements were determined by standard analytical methods in the Analytical Laboratories. With few exceptions, the total percent is 100 ± 0.50 , indicating a high degree of accuracy.

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B. STABILIZATION TREATMENTS (U)

(C) Improvements in both the thermal stability and compatibility of aluminum hydride with other propellant ingredients resulted from this research program. At the beginning of the contract, the most stable hydride that could be produced (without initial gassing) reached 0.1% decomposition in 14 days and 1% decomposition in 50 days at 60°C. By the end of the program, the time required to reach 0.1% decomposition was increased to 40 days, and several samples required over 80 days to reach 1% decomposition at the same temperature. This improvement is illustrated in Figure 12 where area A represents the range of thermal stability of "as received" pilot plant (Texas) AlH_3 with diphenylacetylene (DPA) removed. Area B represents the best stability attained at the beginning of this contract and area C represents the stability resulting from the best treatments developed during this contract period.

1. Development of the pH 7 Stabilization Method (U)

(C) Previous attempts to stabilize aluminum hydride in water had produced erratic results mainly because the reaction rate of the hydride and water was very difficult to control (1). This was due to a rapid rise in pH, which accelerated the hydrolysis reaction (see Section D.3.b.). A slow, controlled hydrolysis was achieved by placing the hydride in a solution buffered at pH 7, thus preventing an increase in alkalinity during the treatment. After the hydride was removed from the buffer and dried, it had a much improved thermal stability and better compatibility with propellant plasticizers. This procedure became known as the pH 7 method of stabilization and is described in Appendix D.

(C) Continued efforts to improve the stability of AlH_3 -1451 by pH 7 hydrolysis treatments at ambient temperature were not successful. In general, thermal stability improved as the oxygen content increased, but no significant deviation from this trend could be produced.

2. Comparison of the pH 7 and 18-Day n-Butylamine Stabilization Methods (U)

(C) The most promising stabilization treatment at the beginning of this research program was an 18-day treatment at 60°C. in n-butylamine containing 2% water. The method was developed under Contract Nr. AF 04(611)-11606 and had produced the most stable hydride at the time. The improvement in stability resulted from a controlled hydrolysis (due to the water in the n-butylamine) of the aluminum hydride and from a beneficial effect of the heat.

(C) Two lots, 02038 and 08187, were compared in order to determine which of the stabilization methods was better. The data from these experiments, presented in Table II, showed that

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Table II

(C) Stability Data for Lots 08187 and 02038 (n-Butylamine and pH 7 Hydrolyzed)

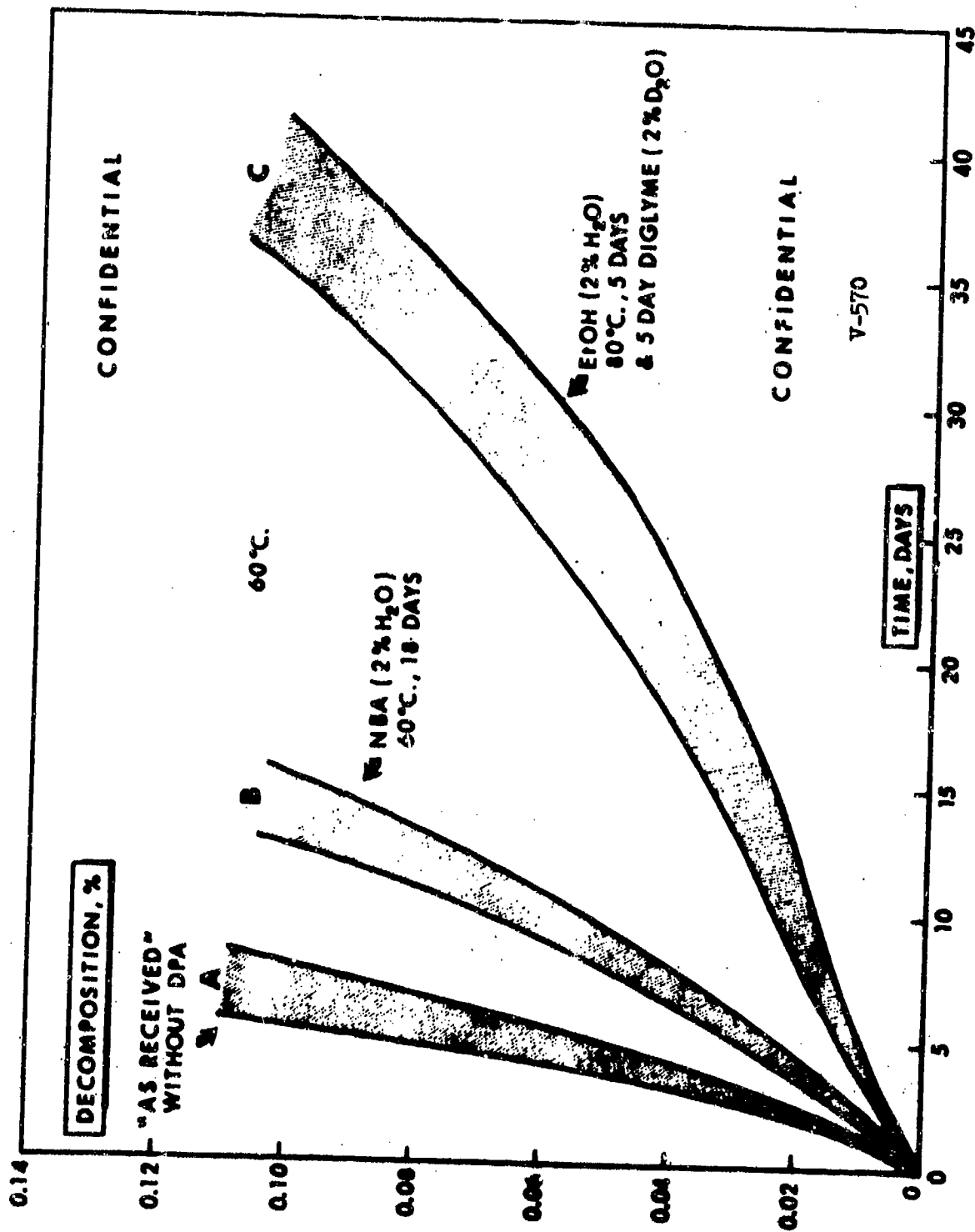
Parameter	As Rec'd	Duration of Treatment									
		n-Butylamine			pH 7 Hydrolysis, days						
		12	18	days	1	2	3	5	7	10	
Lot 08187											
Drying ^a Procedure, hr. at 60°C.	None	0.5	1		0.5	1	0.5	1	16	16	
Initial Gassing at 100°C., %	0.007	0.006	0.004		0.007	0.009	0.012	0.009	0.005	0.004	
Stability, hr. to 0.1% at 100°C.	3.6	4.0	4.4		4.4	4.6	4.4	4.6	5.2	5.5	
Stability, days to 1% at 60°C.	34	62	70		60	60	60	73	82	102	
Oxygen, %	0.36	0.49	0.62		0.61	0.75	0.72	0.90	1.35	1.72	
Lot 02038A											
Drying ^a Procedure, hr./°C.	None	16/25	0.5/60		16/25	--	0.5/60	1/60	1/60	16/60	
Initial Gassing at 100°C., %	0.005	0.004	0.007		0.010	--	0.008	0.011	0.009	0.004	
Stability, hr. to 0.1% 100°C.	2.2	2.75	3.1		2.9	--	3.7	4.0	4.6	5.0	
Stability, days to 1% at 60°C.	15	50	51		37	--	54	61	75	90	
Oxygen, %	0.43	1.13	1.07		1.01	--	1.20	1.41	1.84	2.14	

^a Dried in a Rotovac drier.

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(U) FIG. 12 - Summary of Progress in Improving the Thermal Stability of Aluminum Hydride-1451 Data by 60°C. Taliani Method

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(1) a three- to five-day pH 7 treatment resulted in approximately the same degree of improvement in thermal stability as the 12-18 day NBA (H_2O) treatment, (ii) the increase in oxygen content was less for the NBA-treated material than for any of the pH 7 samples except the one-day hydrolysis, (iii) longer hydrolysis times (7-10 days) in the pH 7 solution increased the thermal stability, but the samples contained appreciably more oxygen, and (iv) the NBA treated samples were easier to dry than the pH 7 samples.

3. Improvement of the n-Butylamine Method (U)

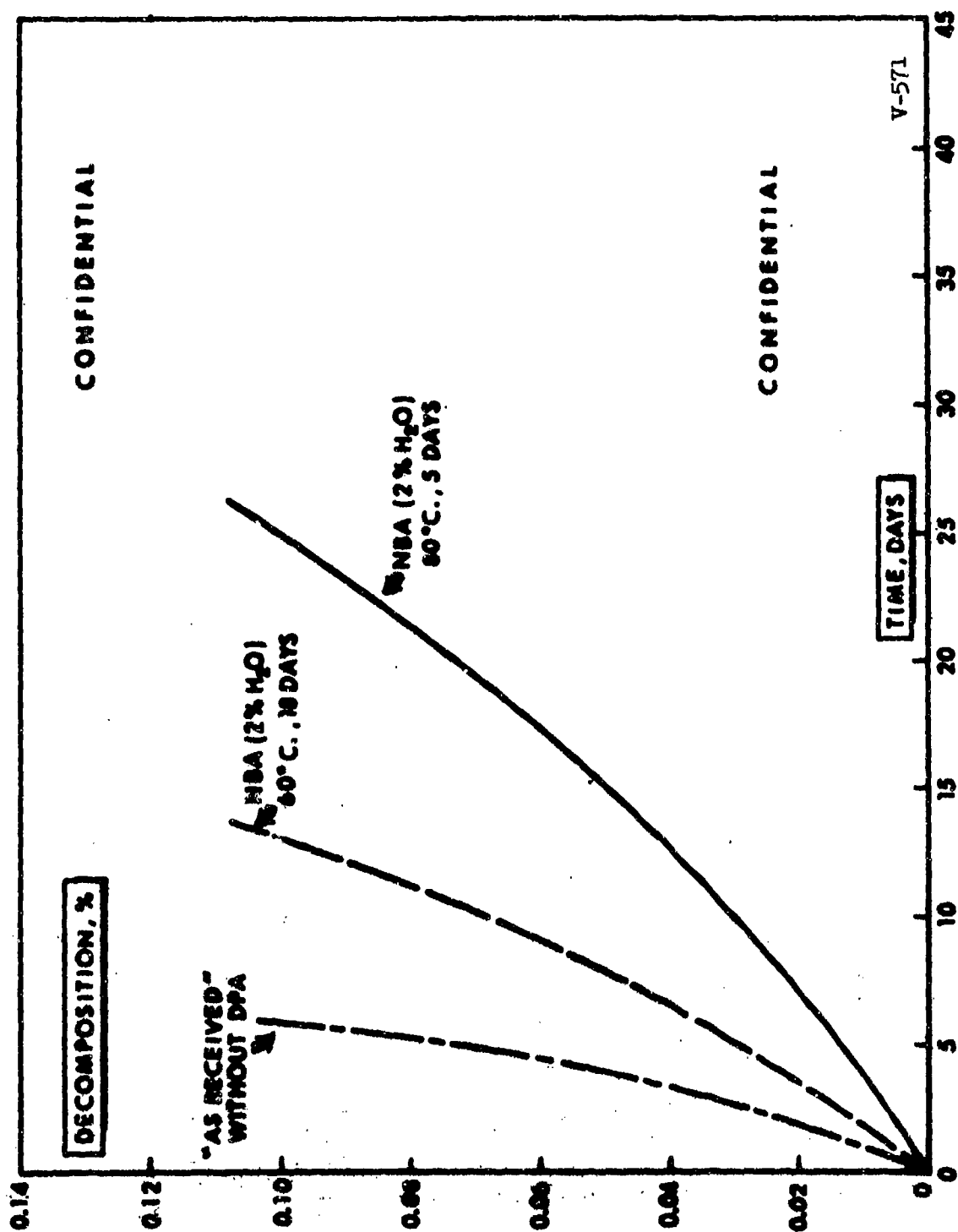
(C) The effectiveness of the NBA treatment was improved by changing both the time and temperature of the treatment. n-Butylamine boils at $77.8^{\circ}C$. If the bath temperature is maintained at $80^{\circ}C$. during the treatment time, there is a gentle reflux of the n-butylamine; this provides a moderate agitation of the hydride. Also, since the temperature is higher, reaction rates are faster, and a shorter treatment time is required.

(C) By maintaining a pot temperature of $80^{\circ}C$. and reducing the treatment time to five days, a significant improvement in thermal stability was obtained without increasing the oxygen content of the aluminum hydride. A comparison of the two NBA treatments at 60° and $80^{\circ}C$. is shown for Lot 11177 in Figure 13. The twofold increase in stability obtained by the higher temperature treatment resulted without appreciably increasing the oxygen content (1.07% for $60^{\circ}C$. vs. 1.15% for $80^{\circ}C$.). From these experiments it was concluded that the heat treatment, as well as the hydrolysis, contributed to the increased stability.

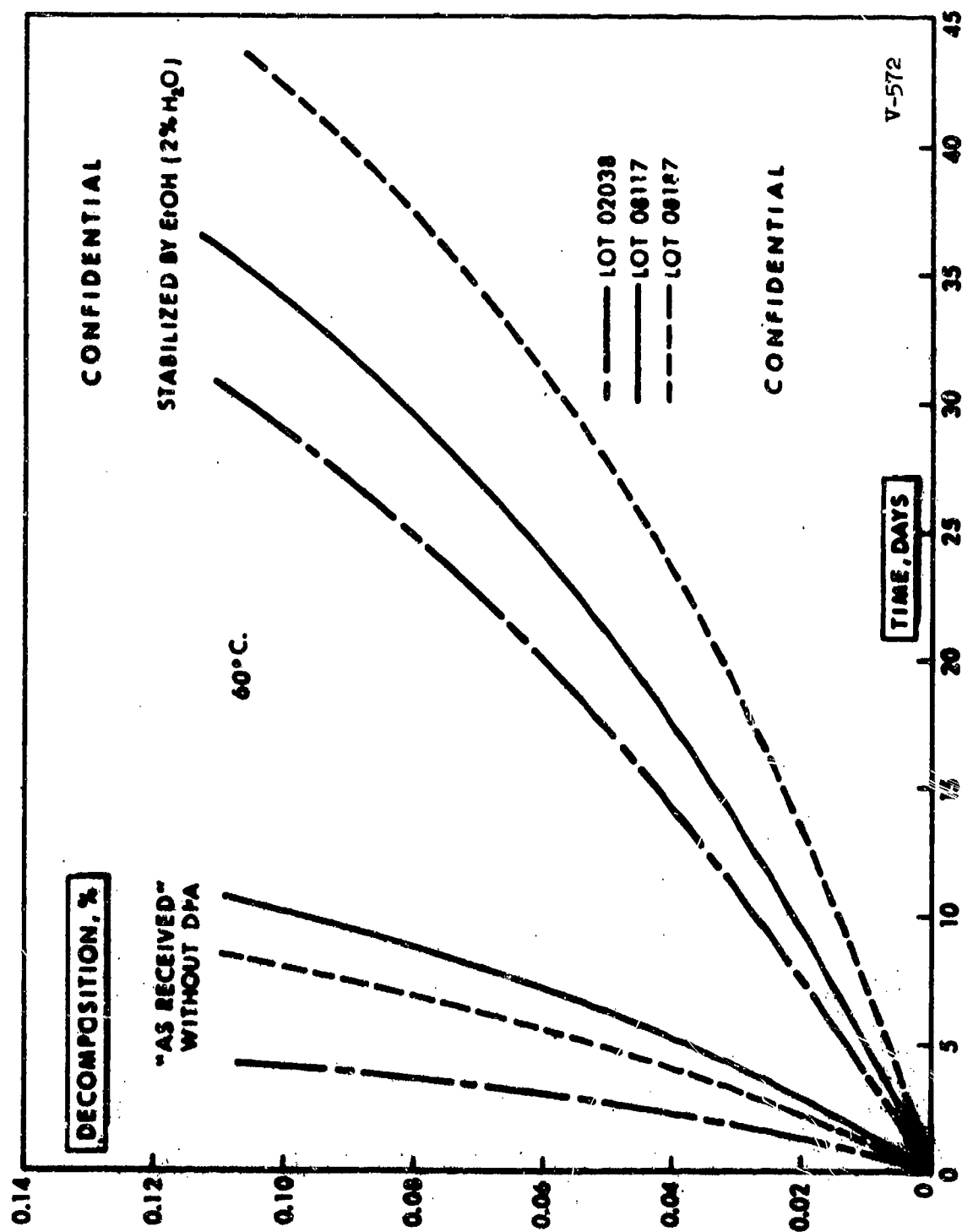
4. Stabilization by Ethanol-2% Water at $80^{\circ}C$. (U)

(C) A number of organic solvents containing 2% water were tested to establish their effectiveness in stabilizing aluminum hydride (Section 6). One of the most promising of these was ethyl alcohol. It boils at $78.5^{\circ}C$., so, like n-butylamine, a mild reflux is maintained at a bath temperature of $80^{\circ}C$. Samples treated in ethyl alcohol containing 2% water at $80^{\circ}C$. for five days showed the best improvement in thermal stability of any method to date. Figure 14 shows the time required to reach 0.1% for Lots 02038, 08187 and 08117 at $60^{\circ}C$. The oxygen content of the treated material was 1.63%, 1.08% and 1.94% respectively. Although not excessive, these values are considerably higher than those obtained by the 5-day NBA treatment. Compatibility tests with TVOPA also showed that the ethanol-treated material produced more initial gassing with TVOPA than either the pH 7 or NBA-treated materials (Section B.6).

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(c) Fig. 13 - Comparison of 60°C. and 80°C. NBA-Treatments of Lot 11177 by Taliani Method at 60°C.

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(C) Fig. 14 - Stability Improvement Resulting from 5-Day 80°C. Treatment in Ethanol (2% Water) by Taliani Method at 60°C.

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5. Exploratory Work With bis(2-Methoxy)diethyl Ether (Diglyme) as the Inert Solvent (U)

(C) A third organic solvent, bis(2-methoxy)diethyl ether with 2% water, was used to treat several lots of aluminum hydride. The stability improvement was equivalent to that obtained with ethanol.

(C) A combination 3-day pH 7 treatment followed by a 5-day treatment in diglyme containing 2% D₂O produced two hydride samples which required 34 and 39 days to reach 0.1% decomposition at 60°C. The oxygen contents were 2.6% and 2.1%, respectively. Prepared late in the program, there was not time to determine the compatibility of these samples with TVOPA.

6. Comparison of Hydrolysis Stabilization Techniques (U)

(C) Four controlled hydrolysis treatments were evaluated for thermal stability and compatibility with TVOPA and TEGDN. Lot 02038 was used throughout these experiments and the treatments selected were as follows:

- (i) pH 7 Hydrolysis (pH 7): The aluminum hydride was treated in an aqueous solution for 7 days at ambient temperature (see Section B.1).
- (ii) n-Butylamine containing 2% water (NBA): The treatment was for 5 days at 80°C. (see Section B.3.).
- (iii) Ethanol containing 2% water (Ethanol): The treatment was for 5 days at 80°C. (see Section B.4.).
- (iv) Acrylonitrile containing 2% water (AN): The treatment was for 18 days at 60°C. This treatment, an extension of earlier AN treatments which were shorter in duration, was included because of its proven effectiveness in improving the compatibility of the hydride with propellant ingredients.

(C) Four criteria were used to evaluate the effectiveness of each of the stabilization treatments:

- (i) Improvement in thermal stability at 60°C.
- (ii) Ease of drying (as measured by initial gassing) after treatment.
- (iii) Oxygen uptake resulting from the treatment.

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- (iv) Compatibility (measured by gas generation rates) of the treated material with two plasticizers, triethylene glycol dinitrate (TEGDN) and 1,2,3-tris[1,2-bis(difluoro-aminoethoxy)-propane] (TVOPA) at 60°C. These were used as 50-50 mixtures with the hydride.

(C) The first lot to be evaluated by each of the four methods was Texas pilot plant Lot 02038 (magnesium-doped). This material required 15 days to reach 1% decomposition at 60°C. before treatment. The oxygen content (indicating degree of hydrolysis) and stability data for the "as received" and stabilized material are shown in Table III. The gas generation rates to 0.10% in TEGDN and TVOPA are shown in Figures 15 and 16, respectively. Similar results are shown for the 0-1% range in Figures 17 and 18. Each sample was rated according to the four criteria previously stated. The treatments were ranked as follows:

(i) Oxygen Uptake

NBA < EtOH < pH 7 < AN

Increasing Oxygen →

(ii) Ease of Drying

NBA = EtOH < pH 7 < AN

Increasingly Difficult →

(iii) Thermal Stability

EtOH > NBA > pH 7 = AN

Decreasing Stability →

(iv) Compatibility

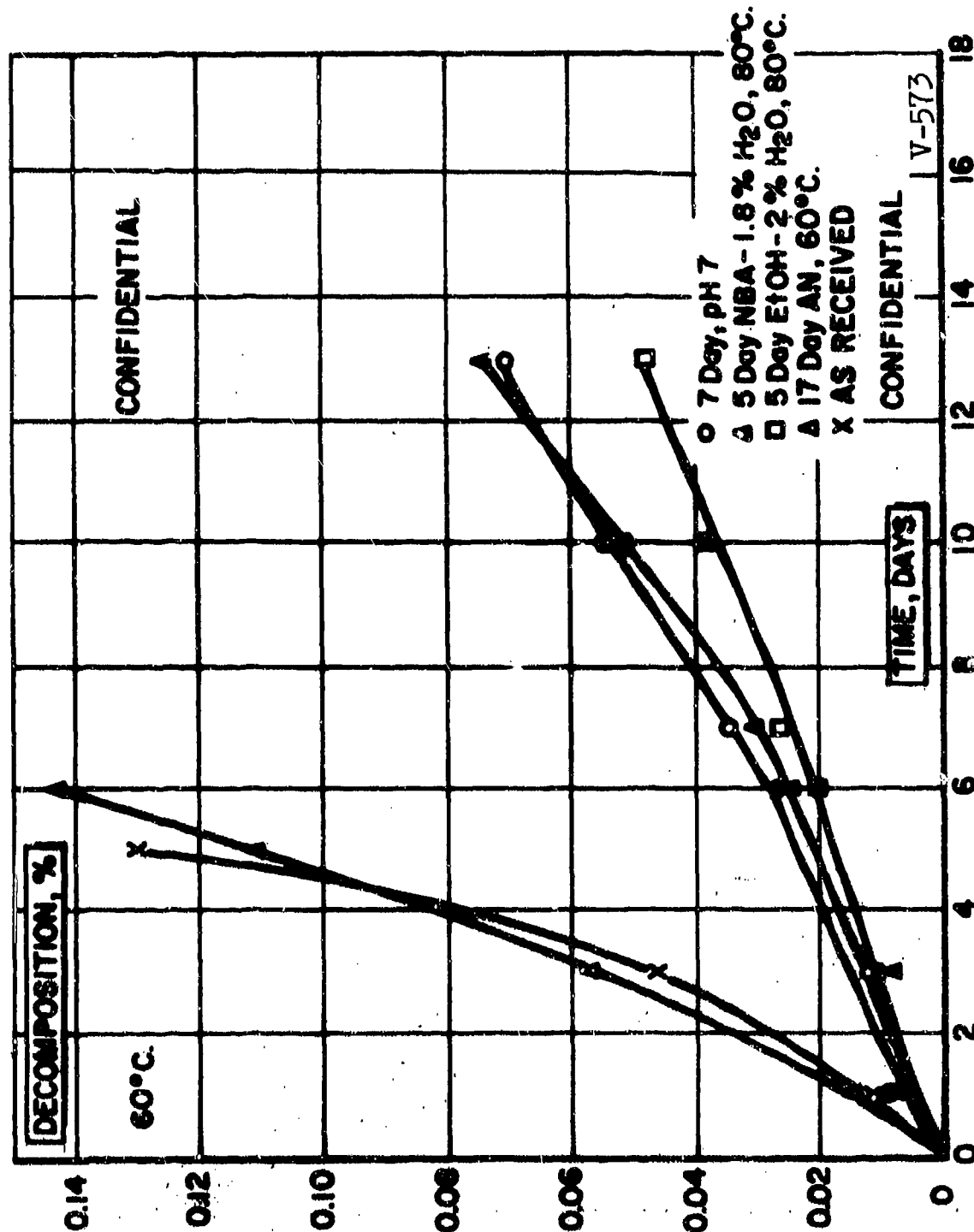
pH 7 > NBA > EtOH > AN

Poorer Compatibility →

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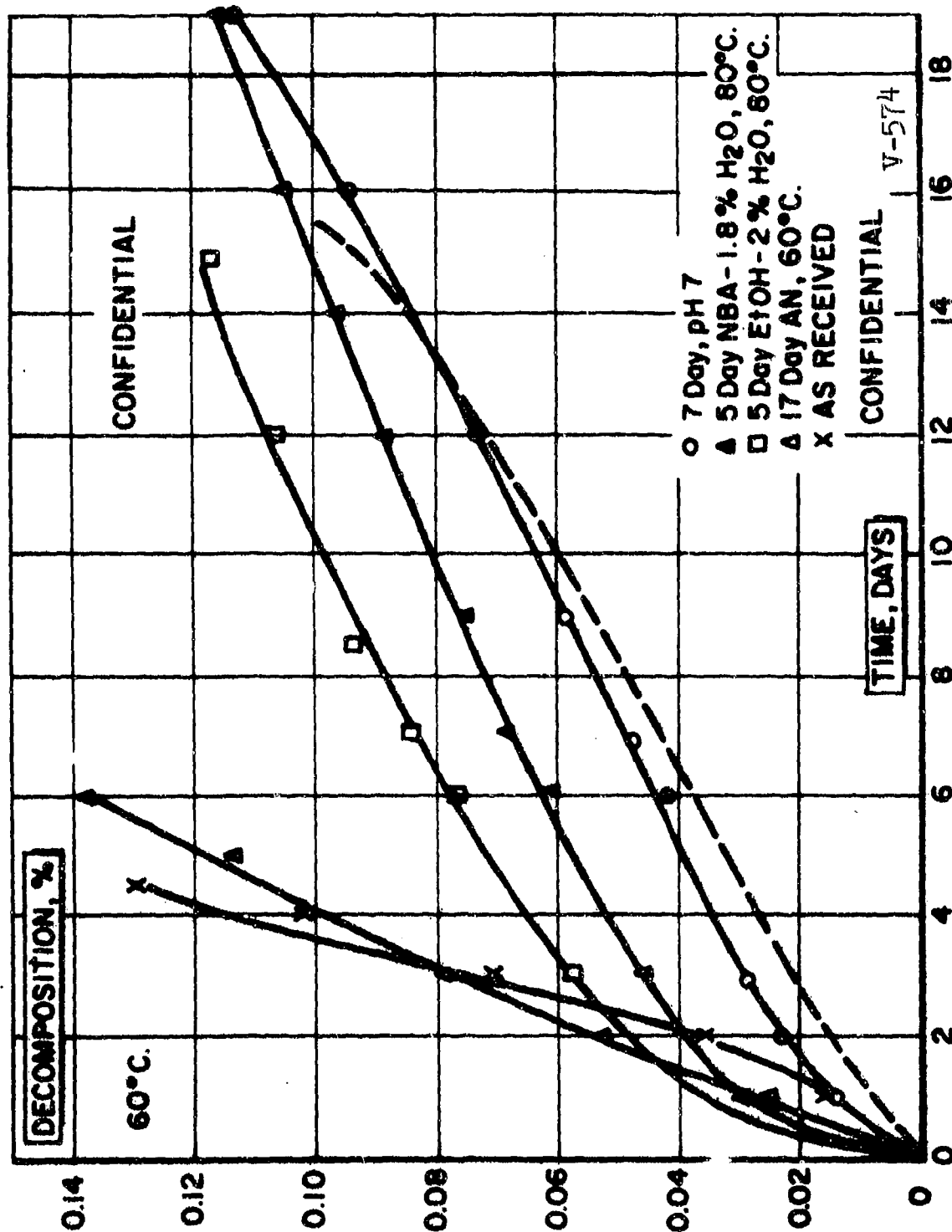
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(C) FIG. 15 - Thermal Stability of Lot 02038 in TEGDN at 60°C. (Taliani)

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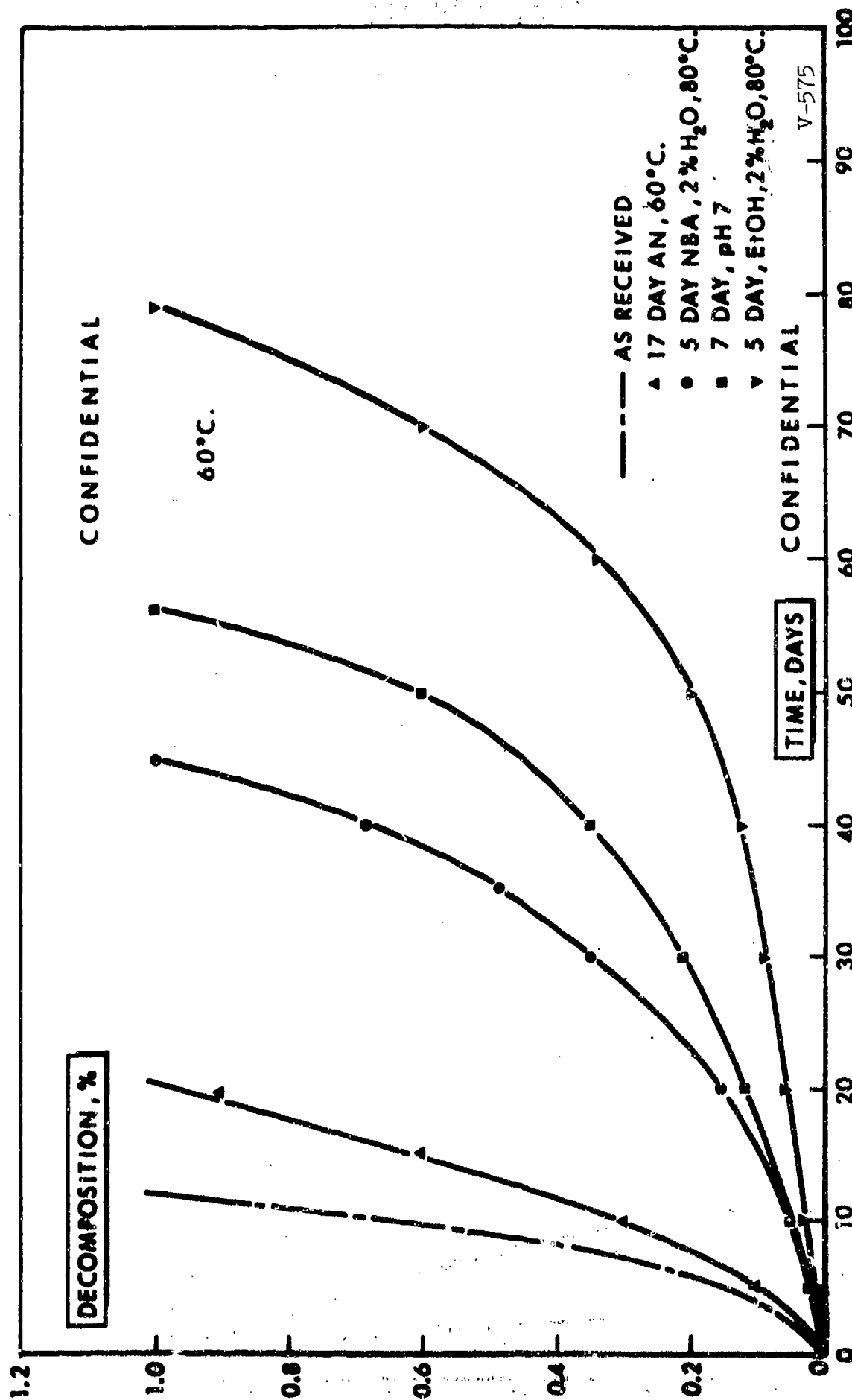


(C) Fig. 16 - Thermal Stability of Lot 02038 in TVOPA at 60°C. (Tallian)

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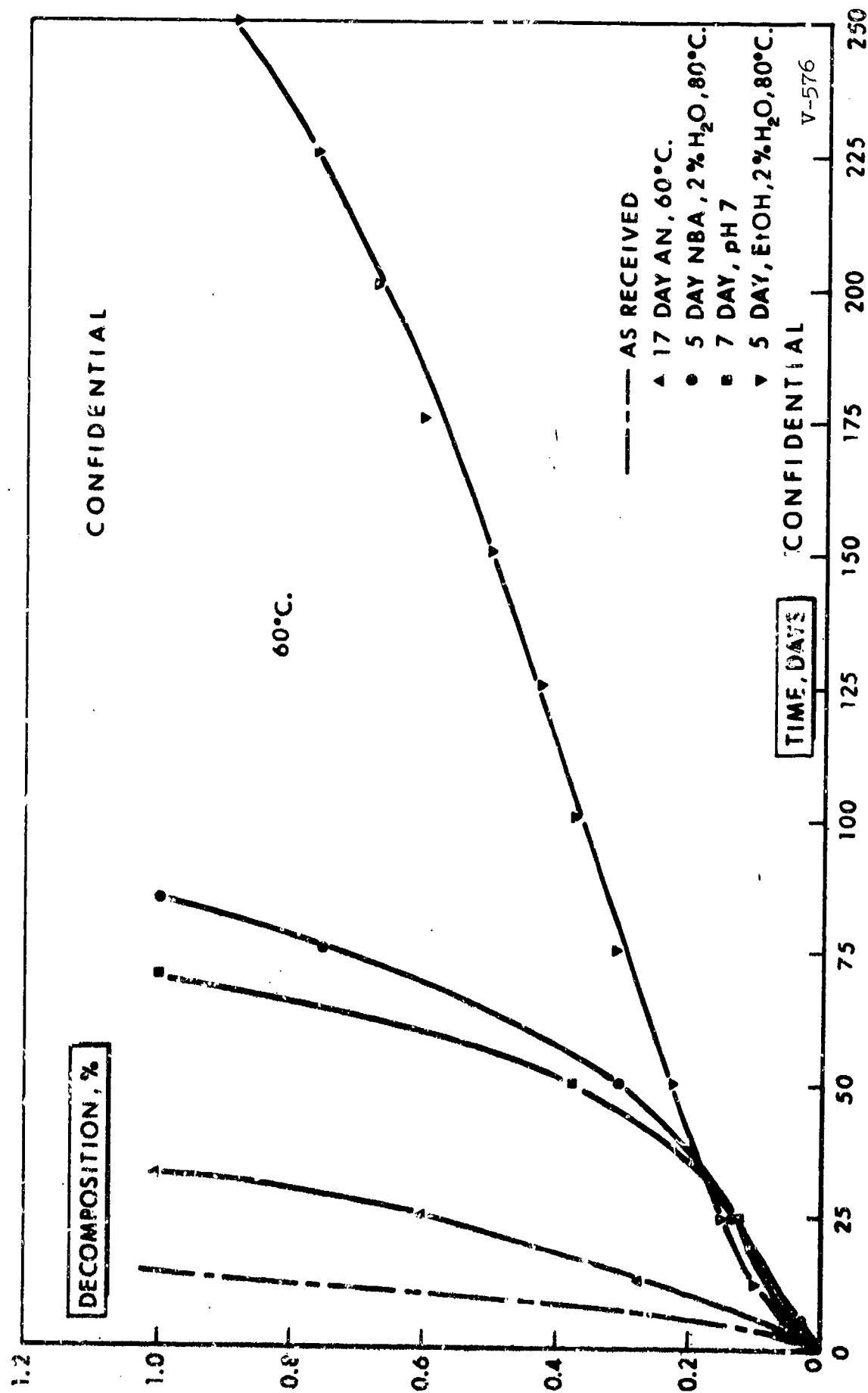
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(c) Fig. 17 - Thermal Stability of Lot 02038 in TEGDN at 60°C. by Taliani Method (0-1%)

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(C) Fig. 18 - Thermal Stability of Lot 02038 in TVOPA at 60°C. by Taliani Method (0-1%)

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Table III

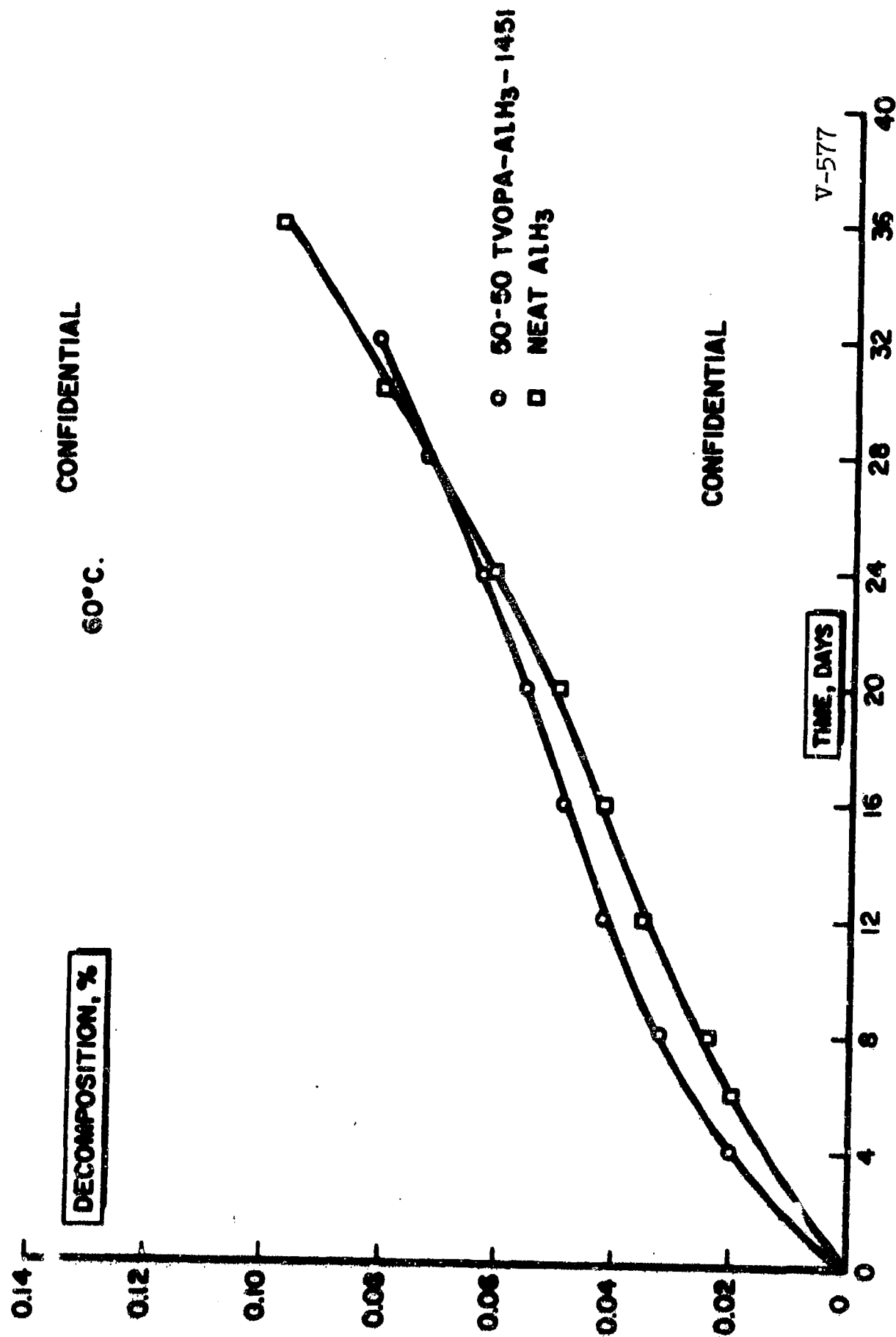
(C) Oxygen Content and Stability Data for "As Received"
and Stabilized Lot 02038

<u>Parameter</u>	<u>As Received</u>	<u>Hydrolyzed 7 Days, pH 7</u>	<u>17-Day AN, 60°C.</u>	<u>5-Day NBA 80°C.</u>	<u>5-Day EtOH 80°C.</u>
Percent Oxygen	0.43	1.84	4.3	1.18	1.63
Stability, Days to 0.1% at 60°C.	3	16	17	20	29
Stability, Days to 1.0% at 60°C.	15	60	44	45	64

(C) A summary of results for each treatment follows:

- (i) None of the four treatments ranked first in each category, although the NBA-treated hydride was first in two of the criteria and second in the other two.
- (ii) The ethanol-treated hydride possessed the best thermal stability, but ranked below the pH 7 and NBA treatments in gas generation rate in 50-50 hydride-TVOPA mixtures.
- (iii) The pH 7-treated material ranked below the ethanol and NBA-treated hydride in thermal stability, but demonstrated the best compatibility with TVOPA.
- (iv) The AN-treated material ranked last in each of the categories.

The excellent thermal stability of the ethanol-treated material and the good compatibility resulting from the pH 7 hydrolysis suggested a combination pH 7-ethanol treatment which would produce a hydride with both the best thermal stability and compatibility. Accordingly, a sample of Lot 02038 was hydrolyzed for 3 days in pH 7 solution and further treated for 5 days in ethanol (2% H₂O) at 80°C. This sample contained 1.55% oxygen and required 36 days to reach 0.1% decomposition at 60°C. Its compatibility with TVOPA (purified by an ion exchange column) is shown in Figure 19. Thus, of all the treatments, this combination produced the most

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(c) Fig. 19 - Gas Evolution Rate of a 50-50 Mixture of Combination Treated [3 day pH 7-5 day EtOH (2% H₂O at 80°C.)] Lot 02038 and TVOPA at 60°C. by Taliani Method

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thermally stable and least reactive material with TVOPA. This was confirmed by similarly treating other lots of hydride. In all cases, however, the oxygen content of the combination treated material ranged between 1.5 and 2%, which was higher than for NBA treated material.

(U) After 37 days at 60°C., the off-gases from the Taliani tubes of the 50:50 mixtures of TVOPA and hydride were analyzed by mass spectrometry. Other than nitrogen, the main component was hydrogen with small amounts of benzene and methylene chloride. Small unidentified peaks also occurred at masses 44 and 81. Completely absent in the mass spectrum were water, hydrogen fluoride and silicon tetrafluoride.

7. Preparation of Stabilized AlH_3 -1451 for Laboratory and Propellant Evaluation (U)

(C) In the early part of July, 1969, Dow agreed to treat pound quantities of aluminum hydride for evaluation by Lockheed Propulsion Company in Domino propellant formulations. The purpose of this program was to answer the following questions:

- (i) Is magnesium-doped hydride necessary for a thermally stable propellant, and, more specifically, is magnesium-doped hydride compatible with NF compounds in the high energy propellant formulations of current interest?
- (ii) What hydride treatment produces the best propellant formulation?
- (iii) Is there a correlation between neat hydride analyses including limited compatibility testing (hydride and TVOPA mixtures) and the stability of propellants containing NF compounds?

(C) The hydride to be treated consisted of two blends. Blend I was a mixture of the most stable lots of non-Mg-doped hydride from the Texas pilot plant. Blend II was Mg-doped material with a thermal stability (after removal of DPA) comparable to that of Blend I. Four 3-pound batches of each blend were furnished Lockheed Propulsion Company for evaluation. One 3-pound lot of each blend was untreated, while the other 3-pound lots were treated for (i) 5 days in NBA (2% H_2O) at 80°C., (ii) 17 days in AN (2% H_2O) at 60°C., and (iii) 3 days at pH 7, followed by 5 days in EtOH (2% H_2O) at 80°C. A small amount of D_2O was added to each treatment solvent, to act as a tracer for mass spectrometry analysis of propellant off-gases (by Lockheed).

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(C) Characterization of each lot (a total of eight) included an elemental analysis, examination by scanning electron microscope and metallograph techniques, determination of thermal stability at 100, 60, 40 and 25°C., and compatibility studies with TVOPA at 60°C. (Blend II only). The elemental analyses of all lots from Blend I are shown in Appendix A, Table XI. Table XII, Appendix A, shows the elemental analyses of all lots from Blend II. The increase in oxygen content resulting from the treatments is the most important change in composition. In each blend the NBA treatment resulted in the least oxygen increase, while the AN and combination treatment introduced considerably more, particularly in Blend I.

(C) The thermal stability curves as determined by the Taliani technique are shown in Appendix B (Figures 26-33). These data show that the treatments are more effective for magnesium-doped aluminum hydride than for non-doped material. For example, only a twofold improvement in stability at 60°C. was realized for non-doped aluminum hydride (pH 7-ethanol treated), compared to a sevenfold increase for the magnesium-doped AlH_3 -1451.

(C) The NBA and pH 7-ethanol Blend II materials showed a very much improved thermal stability at all temperatures. The pH 7-ethanol treated aluminum hydride showed a slightly better thermal stability at 60°C., but this was reversed at 40° and 25°C.

(C) The oxygen increase was much less for NBA-treated materials, but the combination pH 7-ethanol treatment showed the best compatibility with TVOPA. Surveillance of samples which have not yet reached 0.1% decomposition is being continued at 40° and 25°C.

8. Stabilization by High Temperature Diphenylacetylene Treatment (U)

(C) Coating aluminum hydride with diphenylacetylene (DPA) was used as a stabilization technique for more than two years (1). Although the mechanism of this stabilization had not been elucidated, it had been shown that DPA is most effective when it is applied to the crystal surface prior to drying, and particularly prior to exposure of the crystals to water. Results from long-term surveillance of the "in situ" DPA surface treated samples revealed that DPA was less effective at lower temperatures (25°C. and 40°C.) than predicted by accelerated stability data (5).

(C) The interaction of aluminum hydride with DPA was investigated using differential thermal analysis. Mixtures of DPA-aluminum hydride behave in a unique manner, since a small exotherm for DPA occurs at the same temperature that the neat hydride decomposes endothermally. The result is an apparent shifting of the maximum endotherm 20° higher. At elevated temperatures, five reaction products were observed: cis-stilbene, trans-stilbene, diphenylethane, and the dimer and trimer (hexaphenylbenzene) of

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DPA. These compounds are found in very small quantities, and the major portion of the DPA remains unchanged. Hydride samples recovered from these mixtures after the exotherm, but prior to the principal decomposition endotherm, exhibited improved stability.

(C) Further studies of the aluminum hydride DPA reaction and a more complete examination of the stabilization phenomenon were conducted by heating 50:50 mixtures of aluminum hydride and DPA at 160°C. and monitoring the gas generation. Typical curves for these mixtures, with decomposition of aluminum hydride measured by the amount of gas evolved at 160°C., are shown in Figure 20. The initial decomposition produces the typical sigmoid curve, but after 5 to 15% decomposition, the hydride remains relatively stable. During this period the hexaphenylbenzene begins to form. Samples of aluminum hydride were recovered from these mixtures during the stable period, and were found to have a corresponding improvement in stability by Taliani tests at 60°C. The time to reach 1% decomposition at 60°C., "as received", and after the heat treatment are also indicated in Figure 20. It is not known why the stabilization occurs at lower levels of decomposition for the poorer stability samples.

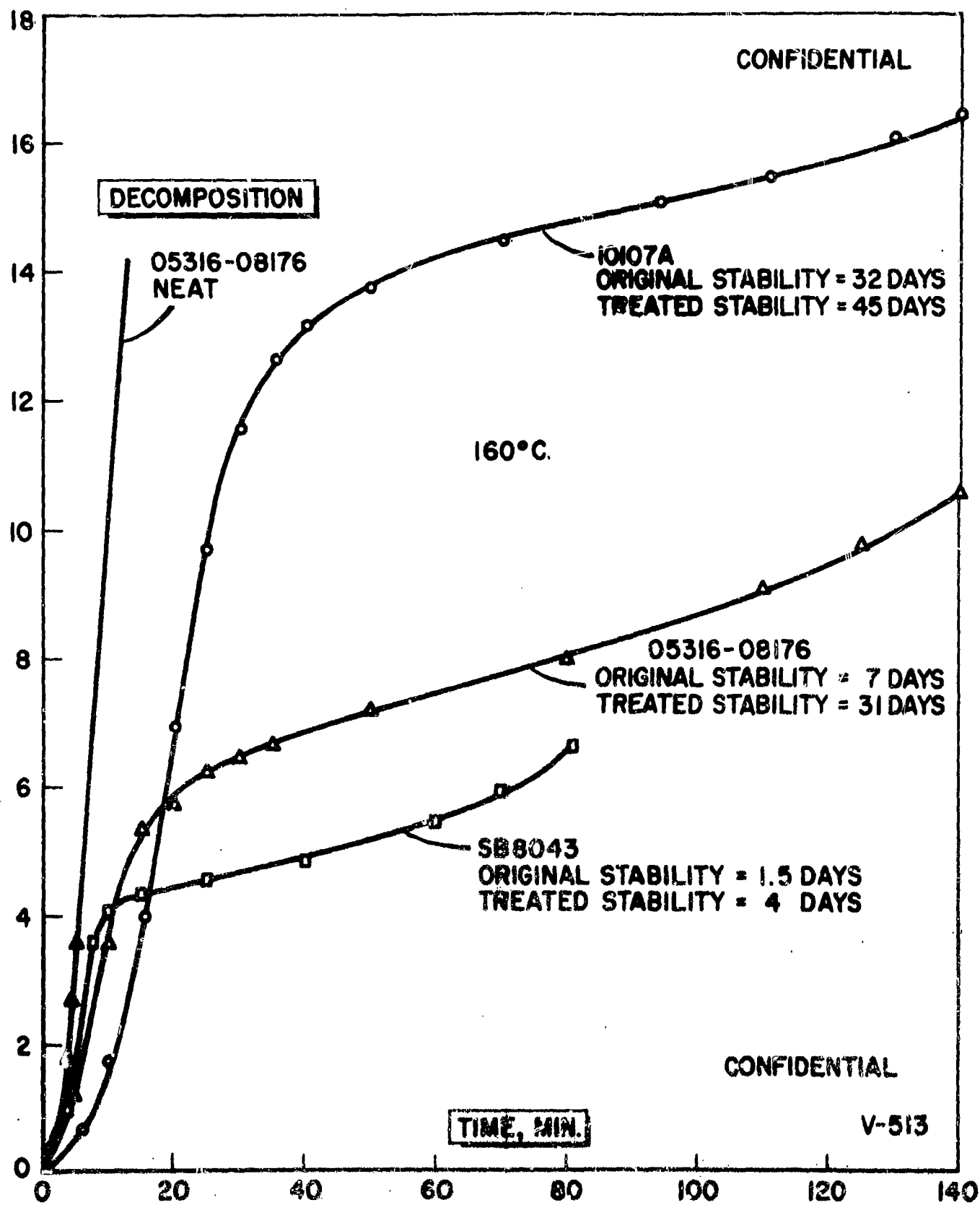
(C) The DPA heat treatment is an alternative technique to hydrolysis stabilization. Energy losses by this treatment are due to the release of approximately 10% of the active hydrogen in the hydride; these losses are approximately equivalent to those resulting from the incorporation of 1.4% oxygen by hydrolysis treatments. Analysis of the DPA-treated hydride has verified that aluminum and aluminum hydride are the remaining components, present in the same ratios as determined by gas generation data during treatment. No compatibility studies were made using material treated in this manner.

C. SYNTHESIS AND PROCESS MODIFICATION (U)

(C) Attempts to make aluminum hydride-1451 from ultrapure reagents have been made in the past (1). In all cases, however, the crystallization step was carried out in a hood. The solution was briefly exposed to air while connecting the flask to the distillation column. The effect of this brief exposure and possible diffusion of air into the system during crystallization was unknown.

1. Preparation of AlH₃-1451 (U)

(C) To eliminate any possible exposure of the hydride or solvents to air and water, a dual length dry box with tower was assembled and maintained at low oxygen and water levels, 2 ppm and 5 ppm, respectively. Solvents were distilled from lithium aluminum hydride to remove trace amounts of water. All starting materials were purified by either multiple recrystallizations, or, in the case of aluminum chloride, by multiple sublimations. The purification of the starting materials, synthesis of the etherated feed solutions, crystallization of the AlH₃-1451, and storage of the product were all done in the dry box.

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(C) Fig. 20 - Decomposition of AlH_3 -1451 in 50% DPA at 160°C.

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(C) Three small batches (1-2 g.) of AlH_3 -1451 were made from the purified materials by the semi-continuous method. The product from all three runs was white polycrystalline AlH_3 -1451. The stability of one batch (no stabilization treatment) was determined. It required 1.1 and 2.8 hours to reach 0.1% and 1.0% decomposition at 100°C., respectively.

(C) A second batch hydrolyzed at pH 7 for 30 minutes required 1.7 hours to decompose 0.1% at 100°C. This was a significant improvement in stability over the untreated sample (1.1 vs. 1.7 hours), but considerably below the stability of the best material obtained from the Texas pilot plant. There was no indication from these experiments that careful purification of starting materials and total exclusion of oxygen and water would, by itself, lead to a superior product. It was concluded, therefore, that a stabilization treatment was necessary to produce highly stable material, and further efforts were concentrated on finding the best stabilization treatment.

2. Improved Methods for Drying Aluminum Hydride (U)

(C) Aluminum hydride, stabilized by the various hydrolysis treatments described in Section B, releases water under vacuum at room temperature. This condition is undesirable for propellant formulations, so it became necessary to develop better drying methods to follow the stabilization treatments. The degree of drying was measured by the amount of "initial gassing" observed at 100°C. as determined by the transducer method. This method was used to compare the effectiveness of the various drying procedures.

a. Drying at Various Temperatures Under Vacuum (U)

(C) Stabilized aluminum hydride samples were dried under vacuum at 100°C., 60°C., and 45°C. The moisture content was usually lowered to an acceptable level (<0.005% initial gassing) after 30 to 60 minutes of heating at 100°C. in a Roto-Vac drier. However, several samples exhibited a loss in stability due to the high temperature. Drying for two hours at 60°C. was sufficient to dry NBA- and ethanol-treated samples, but longer drying times were usually necessary for pH 7 hydrolyzed samples. Samples dried at 45°C. required 40-70 hours to reach the required degree of dryness.

b. Drying by Chemical and Physical Methods (U)

(U) Attempts to remove water from the hydride by azeotropic distillations from benzene and n-hexane were not successful. A chemical drying agent, 2,2-dimethoxypropane, also failed to remove water adsorbed on the hydride.

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(C) The feasibility of using a warm stream of nitrogen to dry treated hydride was demonstrated. Dry nitrogen, heated to 60°C. by means of a heat gun and circulated rapidly through the sample, reduced "initial gassing" much more rapidly than heating the sample at 60°C. under vacuum. Due to limitations in the capacity of the circulating system, the sample size was limited to 20 grams. This method could be scaled up by using a fluid bed drier.

D. FUNDAMENTAL THERMAL STABILITY AND COMPATIBILITY STUDIES (U)

(U) A concentrated effort was made to understand the fundamental processes involved in aluminum hydride activity, particularly the factors affecting thermal stability and compatibility with propellant ingredients.

1. Thermal Decomposition Studies by Metallographic Analysis* (U)

(C) The decomposition mechanism of aluminum hydride is believed to be similar to that of other solids, i.e., the formation and subsequent growth of aluminum nuclei. Previous metallographic studies had indicated that a concentration of aluminum nuclei formed on the exterior surfaces of polycrystalline material, but it was not known whether the more stable hydride from the Texas pilot plant followed this same decomposition pattern.

(C) Metallographic studies of a number of lots from the pilot plant showed that the formation of nuclei was more evenly distributed throughout the crystal than had been previously supposed, and that the exterior surfaces of cubic crystals contributed no more to nuclei formation than internal regions and in some cases not as much. This is illustrated by cross-sectioning different lots of material, both "as received" and stabilized (Figures 21-24), after 1-3% decomposition.

(C) It can also be seen on close examination of the metallographs that the crystals of hydride are imperfect, and that numerous discontinuities such as microscopic cracks, holes, and grain boundaries exist.

(C) The following characteristic modes of decomposition have been observed at low magnification (200X).

- (i) The formation of aluminum at holes (at the surface) and internal voids (Figure 21).
- (ii) The formation of aluminum at aggregation boundaries (Figure 22).

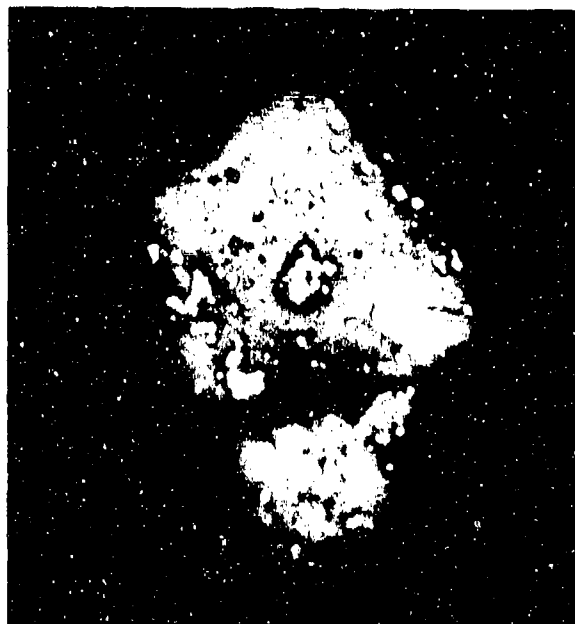
*Metallographs were obtained with the assistance of D. Baker of the Metallurgical Laboratory of The Dow Chemical Company.

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A. 1% Decomposition, 60°C.



B. 1.5% Decomposition, 100°C.



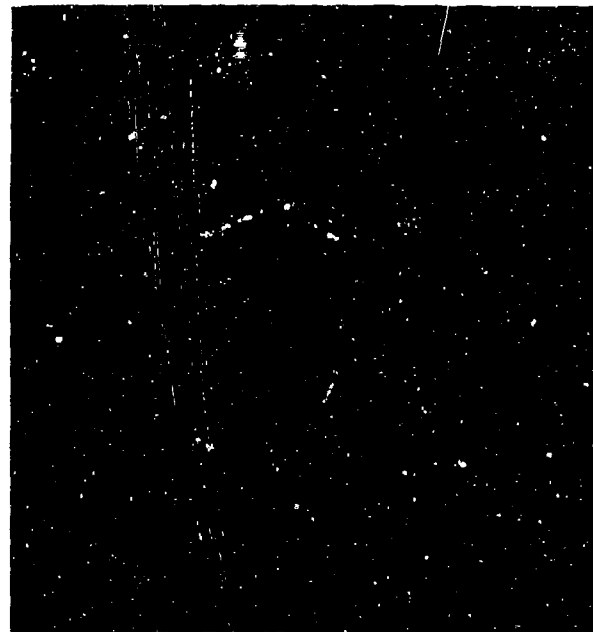
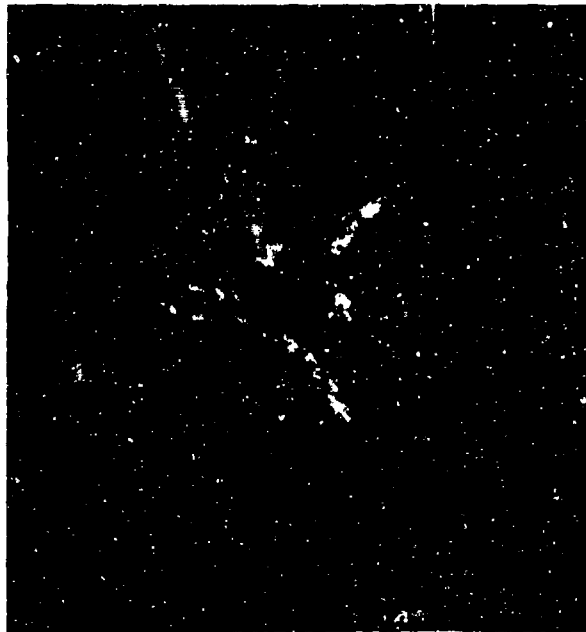
C. 1% Decomposition, 60°C.



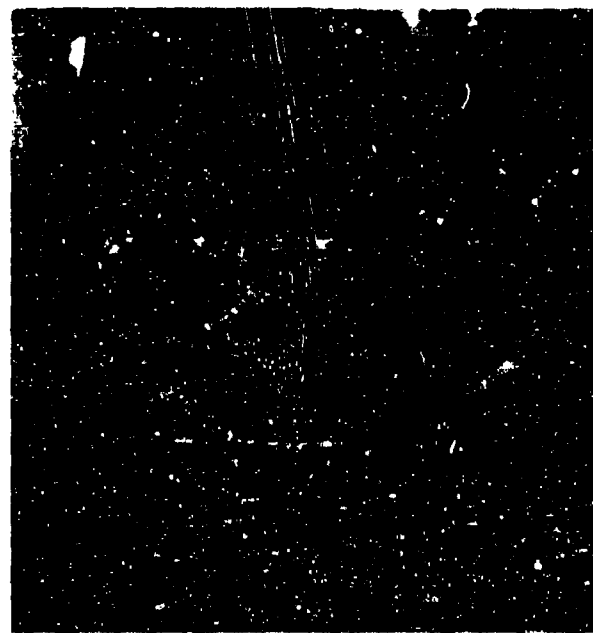
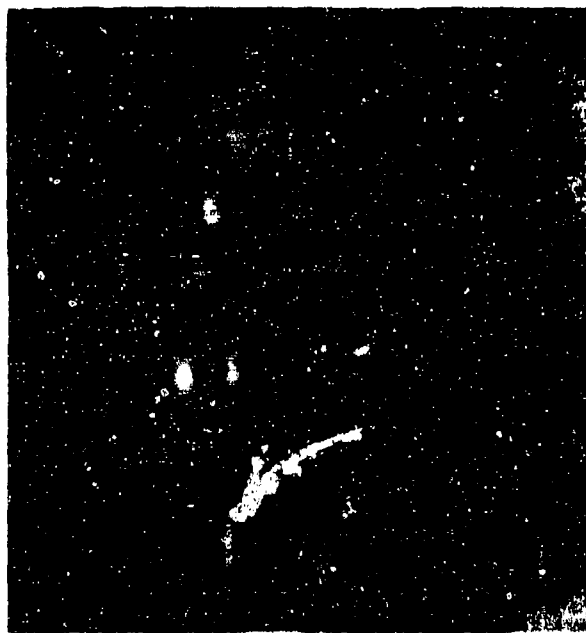
D. 1% Decomposition, 60°C.

(U) Fig. 21 - Metallographs Showing Decomposition
at Holes (on Surface) and Interior Voids

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A. 1.5% Decomposition, 100°C. B. 1.5% Decomposition, 100°C.



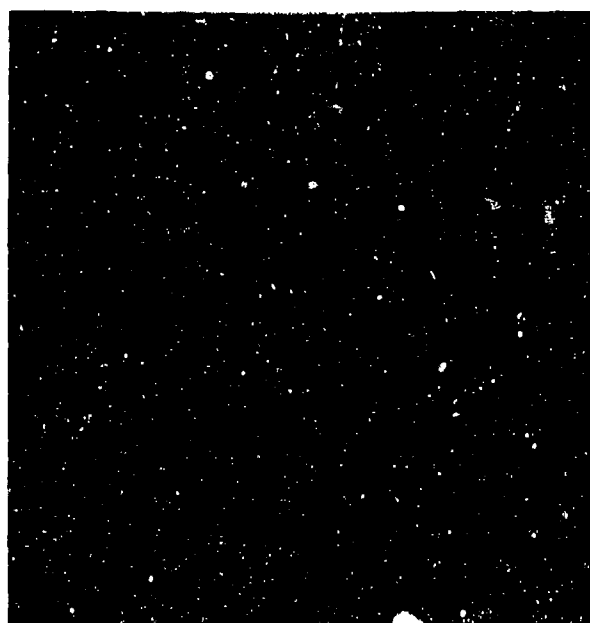
C. 1% Decomposition, 60°C. D. 1% Decomposition, 60°C.

(U) Fig. 22 - Metallographs Showing Decomposition
at Aggregation Boundaries

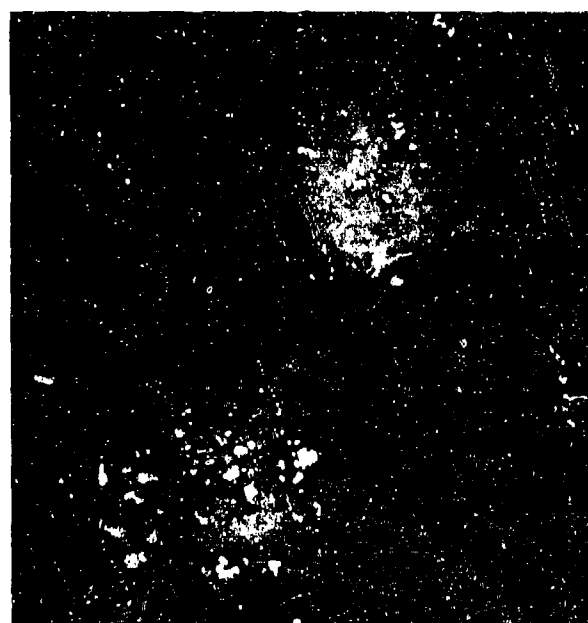
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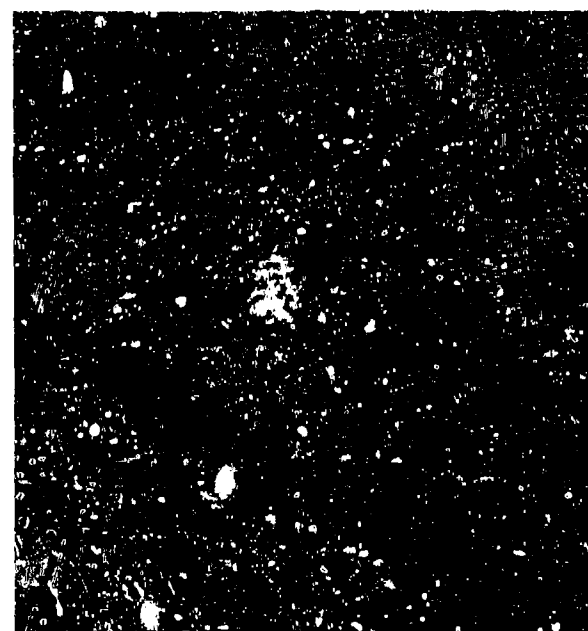
A.



B.



C.



D.

(U) Fig. 23 - Metallograph Showing Decomposition
at Random Site (A, B) and Concentrations
in the Center of Crystals (C, D)

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- (iii) The formation of a single large spot of aluminum in the center of a crystal (Figure 21).
- (iv) The formation of a number of random sites of aluminum (Figure 23, A,B) which for some lots are more concentrated in the center of the crystal (Figure 23, C,D).

(C) Each mode of decomposition is characteristic of a given lot and is not altered by the pH 7 hydrolysis treatment, although at high magnification slight differences can be observed. In "as received" samples, the aluminum forms in discrete pockets having a defined interface with the aluminum hydride. For a hydrolyzed sample, what appears to be an intense pocket of aluminum at low magnification, is observed to be a concentration of very small particles at high magnification. Hydrolyzed samples have also been observed to have a network of fine cracks throughout the crystals. Although the treatment itself may produce these cracks, it appears more likely that the presence of water accentuates existing but invisible cracks. The tendency for these microscopic cracks to become visible during hydrolysis was confirmed by long-term hydrolysis studies. Samples hydrolyzed for 30, 60 and 90 days show the presence of cracks, probably due to increased amounts of aluminum hydroxide formed on their internal surfaces (Figure 24).

2. Identification of Surface Coatings Formed by Hydrolysis Treatments (U)

(U) The scanning electron microscope clearly showed the formation of a surface coating on aluminum hydride crystals (Section A.1.b.). The coatings vary considerably in appearance, and are not always reproducible, even when the same lot is treated by the same method at different times. Smooth coatings (Figure 9F), textured coatings (Figure 9B), and uniform platelets (Figure 8B), have all been observed.

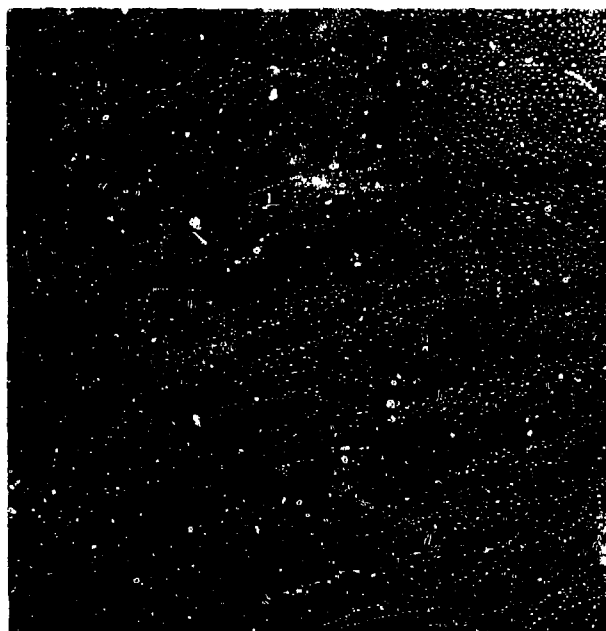
(U) Several diffraction techniques were used in attempts to identify the coatings, particularly the platelets; all were unsuccessful (see Section A.1.b.). It has been noted, however, that the diffraction pattern for AlH_3 -1451 is always seen, but the thicker the coating, the more intense the beam must be to detect it. This suggests that in spite of their appearance under the microscope, the coatings are mainly amorphous aluminum hydroxide.

(U) The helium densitometer was used to estimate the density of the oxygen-containing layer on AlH_3 -1451 crystals resulting from pH 7 hydrolysis. The density was determined before and after treatment; the oxygen content was determined by neutron activation analysis. Assuming that the densities of the surface layer and the hydride are additive, the density of the surface layer was calculated to be 2.0 g./cc.

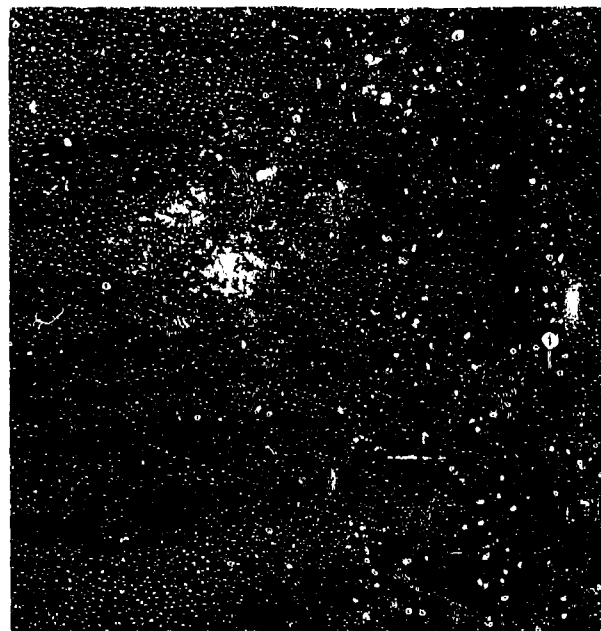
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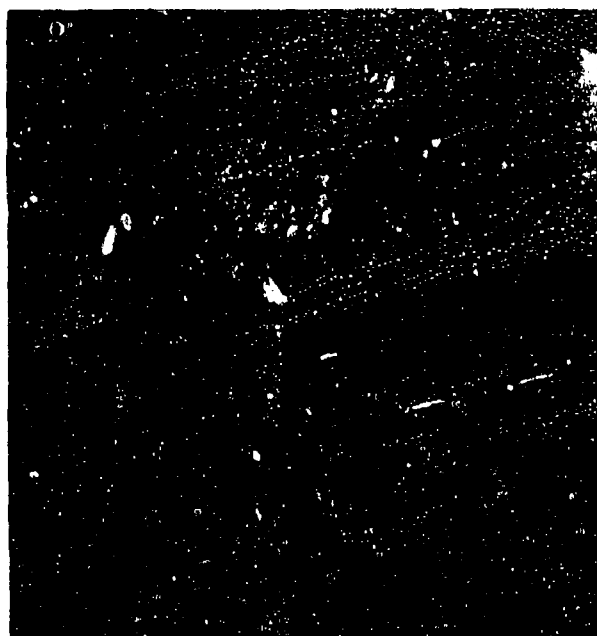
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A. 29 Days



B. 60 Days



C. 90 Days

(C) Fig. 24 - Metallographs of Lot 02038
Hydrolyzed for 29, 60 and 90 Days,
in pH 7 Buffer

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(U) The most probable products from the hydrolysis of aluminum hydride are (i) bayerite, the crystalline form of $\text{Al}(\text{OH})_3$ having a density of 2.4 g./cc., (ii) two crystalline forms of the monohydrated aluminum oxide, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, having densities of 3.3 and 3.5, and (iii) aluminum oxide, Al_2O_3 , having a density of 3.9. Of these possibilities, the density of bayerite is in best agreement with the experimental density (2.4 vs. 2.0), indicating that the surface layer is either bayerite and/or amorphous $\text{Al}(\text{OH})_3$ with a density slightly less than that of bayerite.

(U) A further confirmation that aluminum hydroxide is the surface coating was shown by an extensive hydrolysis of a sample from Lot 08176. The hydride was allowed to remain in water (uncontrolled pH) for twelve hours, followed by drying at reduced pressure. X-Ray analysis of the product showed AlH_3 -1451 to be the chief constituent with 20-30% bayerite present. An elemental analysis showed the following composition: aluminum, 58.4%; hydrogen, 6.76%; magnesium, 0.85%; chlorine, 0.29%; lithium, 0.21%; oxygen, 36.1%. On the basis of percent oxygen, and assuming all the hydrolyzed material to be $\text{Al}(\text{OH})_3$ (crystalline and amorphous), the total amount of $\text{Al}(\text{OH})_3$ was 58% with 42% AlH_3 -1451 remaining; the theoretical amount of total hydrogen for this mixture is 6.45%, which agrees closely with the hydrogen content found by analysis (6.76%). If an appreciable amount of the hydride had been converted to Al_2O_3 during the hydrolysis and subsequent drying, the total hydrogen content would have been much lower.

3. Identification of Impurities in Aluminum Hydride (U)

(C) It is important to know the effect of impurities on the thermal stability and compatibility of aluminum hydride, since the hydride cannot be purified by any known method of recrystallization.

a. Lithium Chloride (U)

(U) Part of the lithium and chloride content of Texas pilot plant lots is due to the presence of lithium chloride. This impurity appears on the surface of the crystals and can be removed by an aqueous wash buffered at pH 7. For example, Lot 10107, "as received", has a chloride content of 0.24% and a lithium content of 0.13%. After being in contact with the water for 10 minutes, the total amount of lithium and chloride in the wash solution was determined. On the basis of the original weight of hydride, the wash removed 0.22 and 0.04% by weight of chloride and lithium, respectively. Thus, approximately 90% of the chloride was removed. The molar ratio (approximately 1:1) of the elements in the water wash corresponds to that of lithium chloride. No appreciable improvement in thermal stability was obtained by the removal of the lithium chloride as described above. It has been concluded on the basis of these data and similar data from other lots that lithium chloride on the surface of the hydride is inert and has no effect on the thermal stability of the material.

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b. Lithium Aluminum Hydride (U)

(C) There is considerable evidence which indicates that lithium aluminum hydride, an additive necessary for the desolvation of aluminum hydride, influences both the thermal stability of the hydride and its compatibility with propellant ingredients. This influence is illustrated by several related experiments described below.

(1) Generation of Base During Hydrolysis (U)

(C) It was observed that an in situ generation of base occurred when aluminum hydride was placed in water. For example, 10 grams of Lot 08176, a sample unusually high in lithium (0.40%), was washed 3 successive times with 100 ml. of water. The results, Table IV, show that base was released by each wash, and the concentrations of lithium and hydroxyl ion decreased with successive washes.

Table IV

(U) Extraction of Lithium and Hydroxyl Ion by Water Wash

<u>Wash No.*</u>	<u>pH</u>	<u>Lithium Conc. mMolar</u>	<u>Hydroxyl Conc. mMolar</u>
1	11.4	16.4	4.7
2	10.8	4.0	2.0
3	10.2	1.9	1.4

*100 ml. each wash.

(U) The hydroxyl ion concentration represents the amount of lithium hydroxide generated by the reaction of water and lithium aluminum hydride, while the excess lithium is due to soluble lithium chloride. Similar results were obtained for other lots, although the amounts of base, lithium and chloride show wide variations. Hydride which was dried after an uncontrolled hydrolysis showed little or no improvement in hydrolytic stability when placed again in water. If the pH of the water is maintained at 7 during hydrolysis, the reactivity of the recovered hydride with water is greatly reduced. It is concluded that this resistance to hydrolysis is due to a coating of aluminum hydroxide which retards further reaction of water with the hydride.

CONFIDENTIAL(2) Extraction of Lithium Aluminum Hydride From AlH₃-1451 (U)

(C) Since lithium aluminum hydride was the suspected precursor of the strong base (believed to be LiOH) found in the wash water, attempts were made to identify this compound. Previous efforts to increase the stability of AlH₃-1451 by washing with diethyl ether on a Soxhlet extractor had failed (6), presumably because no lithium aluminum hydride was removed. If lithium aluminum hydride was occluded in the aluminum hydride crystal, it did not migrate to the surface of the crystal where it could dissolve in boiling ether. In order to expose the interior of the crystals to ether, fifty grams of Lot 08176 (Li = 0.40%) was ball-milled for one hour to produce a material with particle sizes less than 1 μ . This was followed by an overnight extraction with diethyl ether. After filtering and removing the solvent, 0.4 g. of a white, water-reactive solid, was recovered. X-Ray analysis showed the chief constituent to be lithium aluminum hydride, with smaller amounts of lithium aluminum hydride diethyl ether complex. The lithium content of the extracted aluminum hydride dropped from the original 0.40% to 0.30%. A second overnight extraction with ether produced only a trace of solid material.

(C) The above experiment was repeated in an effort to extract a greater amount of the lithium, analyze for magnesium content, and better characterize the extracted material. Approximately 0.3 g. of a white crystalline solid was obtained. It was identified by both X-ray and IR as lithium aluminum hydride, was soluble in ether, insoluble in benzene, and contained less than 0.3% magnesium. A second one-hour grinding followed by an extraction produced no additional soluble material; the lithium content of the hydride remained practically the same as before the second grinding (0.29% vs. 0.30%).

(C) In order to determine whether the NBA treatment affected the amount of extractable material, 50 grams of the same lot (08176) was NBA-treated for 18 days at 60°C., ground in a ball mill for one hour and extracted with ether. In contrast to the "as received" sample only a very small amount (0.06 g.) of material was extracted, and no lithium aluminum hydride was found by X-ray. It appears, therefore, that the soluble lithium aluminum hydride present in the original material was transformed into an insoluble form which is probably less reactive. These results also explain why a hydrolysis stabilization treatment at elevated temperatures, e.g. 60° and 80°C., is more effective in improving the thermal stability of aluminum hydride than a hydrolysis treatment at room temperature (pH 7). Numerous experiments have shown conclusively that, for the same amount of hydrolysis (measured by oxygen uptake), treatments at 60°C. or 80°C. in both n-butylamine and ethanol are more effective than the pH 7 treatment at 25°C. This beneficial effect at 60°C. or

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80°C. is due to a more effective removal of lithium aluminum hydride by a combination of hydrolysis and thermal decomposition.

(C) During treatment the small amount of water in the solvent prevents growth of nuclei which would proceed unchecked if the neat material were heated in the same manner. The net result is the application of heat with a minimum of decomposition, a more effective removal of lithium aluminum hydride at the higher temperatures, and a seven- to tenfold increase in the thermal stability of the treated hydride.

(C) The results from these experiments led to the following conclusions:

- (1) Lithium aluminum hydride is occluded in AlH_3 -1451 crystals, and is responsible for part of the lithium content of the hydride.
- (ii) Prolonged heat treatments in n-butylamine containing 2% water either hydrolyze or change the lithium aluminum hydride originally present in the material to an ether-insoluble form.
- (iii) Only about 25% of the lithium content can be removed by an ether extraction of ground material. The remaining 75% is either present as an insoluble form, or additional grinding is ineffective in exposing new internal crystal surfaces.
- (iv) A correlation exists between the loss of soluble lithium aluminum hydride and an increase in thermal stability.

(U) Due to the insolubility of aluminum hydride in diethyl ether, there is no penetration of the crystal by ether and, as a result, there is no extraction of lithium aluminum hydride. Water, however, reacts slowly with aluminum hydride even at pH 7, and much faster at high pH values. Unlike ether, water requires but a short time (15-20 seconds) to penetrate the hydride surface where it reacts with lithium aluminum hydride immediately below the surface. The result is an autocatalytic effect, with the hydrolysis of lithium aluminum hydride producing lithium hydroxide, which, in turn, increases the rate of hydrolysis of aluminum hydride. With increasing time, the generation of large amounts of aluminum hydroxide buffers the solution, the pH drops, and the reaction rate is simultaneously reduced.

CONFIDENTIALc. Impurity Identification by Dissolution of AlH_3 -1451 (U)

(U) The only known solvent for AlH_3 -1451 is tetrahydrofuran (THF). The hydride is insoluble in THF if it has been exposed to air and/or water; even a slight coating of aluminum hydroxide makes it completely insoluble.

(C) It was reasoned that lithium and/or magnesium compounds insoluble in diethyl ether might also be insoluble in THF and could be recovered as a residue by dissolving away all of the AlH_3 -1451. Analysis by X-ray and infrared would allow identification of such impurities.

(C) Ten grams of Lot 02038 was ground and dissolved in one liter of THF at room temperature. The remaining insoluble material was a black precipitate which settled to the bottom of the flask and an opaque, white material which remained suspended in the THF. The black precipitate was identified as $\alpha\text{-Al}_2\text{O}_3$ and aluminum. The former can be disregarded since it resulted from the ball mill. The aluminum resulted from the small amount originally present as a decomposition product. The suspended material when dried was amorphous by X-ray analysis and was undoubtedly aluminum hydroxide resulting from hydrolysis of the starting material over a period of time. Thus, no new THF-insoluble species were identified. Similar results were found for freshly made hydride; it completely dissolved, leaving no insoluble residue. The indication that THF dissolves all the lithium and magnesium compounds present was confirmed by analyses of aluminum hydride tetrahydrofuranate recovered by stripping the solvent. It had the same lithium and magnesium content (based on AlH_3) as the original material. (Li:0.19 vs. 0.17%, Mg:1.2 vs. 1.3%.)

(C) These experiments show that all of the magnesium and lithium species incorporated in aluminum hydride are soluble in THF, but it cannot be shown with certainty that they are soluble in diethyl ether. However, if they are highly oxygenated species, such as LiAlO_2 , it is doubtful if they would be soluble in either solvent. It appears more likely that they exist as hydride species which can become solvated and as a result are soluble in THF.

4. Correlations Between Lithium Content and Aluminum Hydride Stability (U)

(C) Evidence that the lithium content and thermal stability of aluminum hydride samples are related was found in computer correlations of the analytical and stability data obtained from material previously produced by the Texas pilot plant. Of nine independent variables studied, four correlated with stability, accounting for 60% of the variation. Of the four, lithium had the largest (negative) correlation coefficient, i.e., low lithium related to high stability, with magnesium having the second

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highest (positive) correlation, i.e. magnesium doping is effective in the semi-continuous process. The other significant variables were yield and rate, indicating that the process was continuously being improved as additional experience was gained. A computer plotting of all the available data for stability versus lithium content, shown in Figure 25, indicates the trend, but the scatter of points shows that lithium content is not the only factor related to thermal stability. The line in Figure 25 is the best straight line which can be obtained by a computer. The points indicate, however, that a curved line similar to the dotted line shown would be more representative of the trend.

5. Effect of Water in Solvents Used for Stabilization (U)

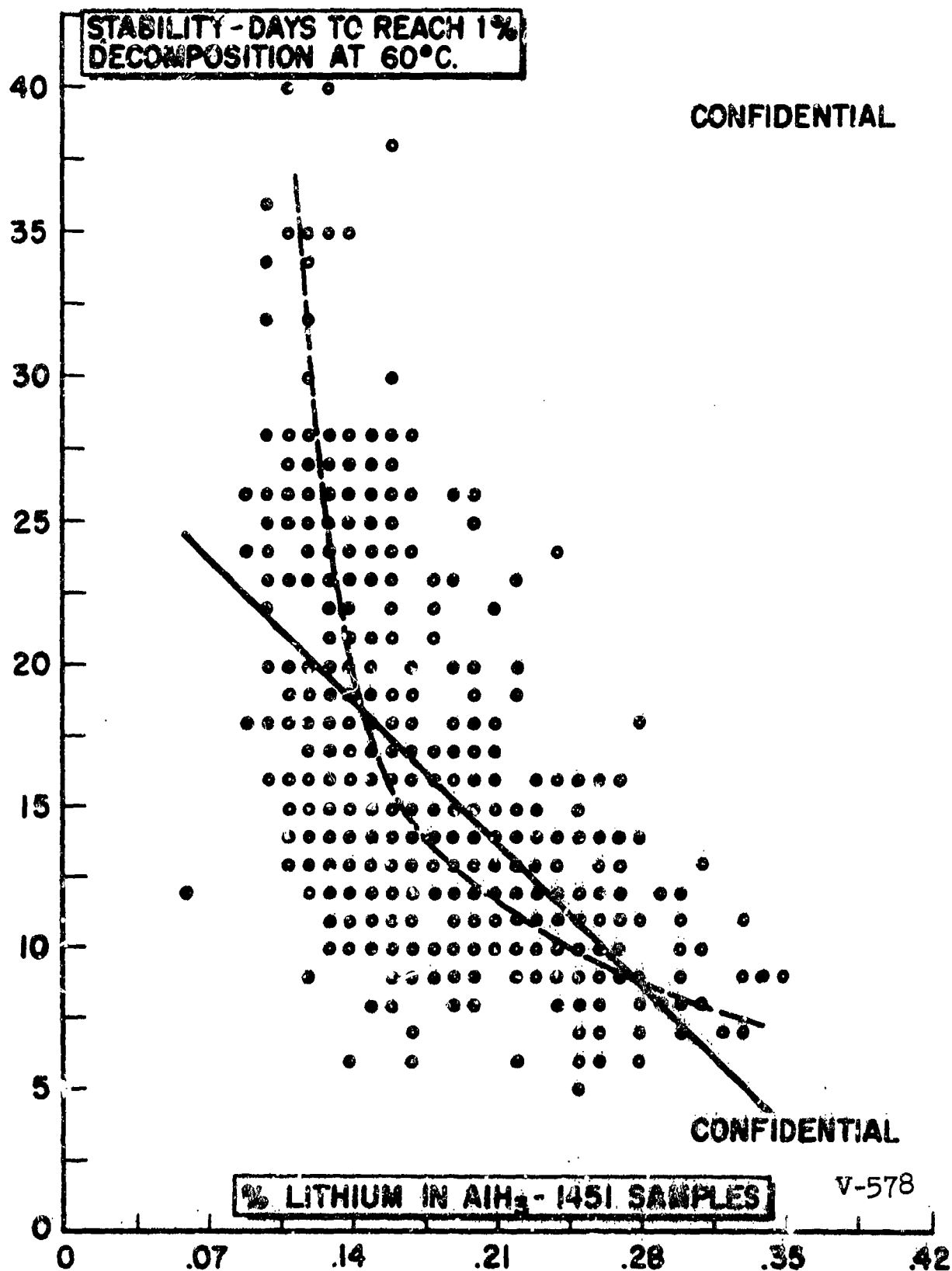
(C) The improvement in stability realized by treating the hydride in wet organic solvents is believed to be due primarily to the presence of small amounts of water (~2%). In order to verify this, four samples from Lot 02038 were treated with acrylonitrile (AN) containing varying amounts of water. The results are shown in Table V. Aluminum hydride from the AN treatment containing 0.05% water (Sample 1) required only 0.4 hour to reach 0.1% decomposition at 100°C. (vs. 2.2 hours prior to treatment). With addition of water to the AN (Samples 2, 3 and 4), both stability and oxygen content increased, although Sample 3 was the only one which showed a better stability than the "as received" material. A similar decrease in stability was observed for material treated in 2B ethanol containing 0.08% water (Sample 5). X-Ray analysis of Samples 1 and 5 (dried solvents) showed an aluminum content of 2-3%, proving that dry organic solvents have no stabilizing effect, with decomposition occurring during treatment.

(C) A sample of AlH_3 -1451 placed in n-butylamine containing 0.10% water reacted with the amine after 48 hours at 80°C. (Sample 6) converting all the amine and hydride into a white solid which was active and hydrolyzed readily. Elemental and infrared analysis of the product indicated that it was probably $(\text{n-Bu})_2\text{Al-N-Bu}$

H

6. Effect of Organic Solvents (U)

(C) Experiments with numerous organic solvents containing low amounts of water showed that some were more effective than others in improving stability. In addition, several organic solvents produced high amounts of oxygen in the hydride without a corresponding increase in stability. It was not known whether these differences existed because of functionality, potential to polymerize, or perhaps an affinity for water. Methanol, in place of ethanol, with 2% water was used in two experiments. Some stability improvement was achieved, but in both cases excess oxygen

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(C) Fig. 25 - Correlation of Lithium Content Versus Stability
for the Texas Pilot Plant Data

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Table V
(U) Thermal Stability of Lot 02038A Sample vs. Water Content
of Organic Solvents

Sample No.	Organic Liquid	H ₂ O in Organic Liquid, %	Treatment Time, days	Stability hrs. to 0.1% Decomp. ^a at 100°C.	Oxygen %	Remarks
1	Acrylonitrile	0.05	18(60°C.)	0.4	0.34	Contains 2-3% alu-minum.
2	Acrylonitrile	0.5	18(60°C.)	1.7	2.05	---
3	Acrylonitrile	2.0	18(60°C.)	2.5	4.32	High oxygen content.
4	Acrylonitrile	2.0	5(80°C.)	1.7	3.70	---
5	2B Alcohol	0.08	5(80°C.)	0.6	0.83	Contains 2-3% alu-minum.
6	n-Butylamine	0.10	3?(80°C.)	---	---	After 48 hrs. the 1451 and NBA had reacted.

^aTransducer data

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(>2.5%) was added. Likewise, dimethylamine, in contrast to n-butylamine, introduced 7.5% oxygen with little improvement in stability over the original material. These results indicated that functionality of the organic solvent is not a reliable criterion for predicting the efficiency of a stabilizing medium.

(C) Experiments with polymers or polymer-forming compounds such as low molecular polyacrylamide and acrylamide monomer in water buffered at pH 7 produced no improvement in stability greater than what would have been obtained by the pH 7 treatment itself. Other solvents (with 2% water) tried without success were acetone, tetrahydrofuran, dioxane, glacial acetic acid and dimethylformamide.

(C) bis(2-Methoxy)diethyl ether (diglyme) with 2% water or deuterium oxide was as effective in stabilizing aluminum hydride as ethanol (2% H₂O). Since it is a higher boiling liquid, it must be removed with an acetone wash prior to drying. Two lots, 02038 and 08217, were treated for 3 days in pH 7 buffer and followed by a 5-day treatment at 80°C. in diglyme containing 2% deuterium oxide. The times required to reach 0.1% decomposition at 60° were 39 and 34 days, respectively. The only disadvantage of the method is the amount of oxygen incorporated into the sample; Lot 02038 after treatment contained 2.1%, and Lot 08217 contained 2.6%. Further work to improve this method is recommended, but large amounts of hydride should not be treated by it until the degree of hydrolysis is reduced.

7. Substitution of Deuterium Oxide for Water in Organic Solvents (U)

(C) Deuterium substituted for hydrogen in the AlH₃-1451 lattice makes a more stable compound (6). It was not known whether a surface coating of Al(OD)₃ would be more effective than Al(OH)₃ in stabilizing AlH₃-1451. In order to determine this, organic solvents which would not exchange hydrogen for deuterium were used. These included dioxane, dimethylformamide and diglyme. Only one sample of each of the first two was run, since in each case high oxygen values resulted. In addition to the results reported in Section D.6 samples from two other lots were treated in diglyme containing 2% deuterium oxide. The improvement in stability was comparable to that obtained using 2% water in diglyme, and, since it appeared that D₂O offered no appreciable advantage over water, no further work with deuterium oxide in organic solvents was done.

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SECTION IV

(U) CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS (U)

(C) Based on the results discussed in this report, the following conclusions are made:

- (i) The thermal and hydrolytic stability of AlH_3 -1451 is improved by a controlled hydrolysis at 80°C . using either n-butylamine or ethanol as the carrier for water.
- (ii) The NBA treatment (5 days at 80°C .) is the preferred treatment at this time. It increases thermal stability by five- to seven-fold, improves the compatibility of aluminum hydride with propellant ingredients, and consistently produces stabilized AlH_3 -1451 with a low oxygen content ($\sim 1\%$).
- (iii) A strong base, probably lithium hydroxide, is generated in situ when AlH_3 -1451 is placed in water. This greatly increases the hydrolysis rate and makes an uncontrolled hydrolysis impractical as a means of stabilizing the hydride.
- (iv) A controlled pH 7 hydrolysis at 25°C . produces aluminum hydride with improved thermal stability and compatibility with propellant ingredients. For the same degree of hydrolysis (as measured by increased oxygen content), it does not increase the stability as much as the wet NBA or ethanol treatments at higher temperatures.
- (v) A treatment consisting of a 3-day pH 7 hydrolysis, followed by a 5-day ethanol (2% H_2O) reflux at 80°C ., produces hydride with the best compatibility in a 50:50 aluminum hydride/TVOPA mixture. A disadvantage is the higher oxygen content of the AlH_3 -1451 after treatment (2% vs. 1% for NBA-treated hydride).
- (vi) Stabilization treatments are much more effective for magnesium-doped aluminum hydride than for non-doped material.

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- (vii) Lithium aluminum hydride is present as an impurity in aluminum hydride and is probably responsible for initiating decomposition.
- (viii) Unstable aluminum hydride samples show a higher surface lithium concentration than those possessing good stability. Surface concentrations of lithium are, in general, higher than the concentration in the crystal interior.
- (ix) The lithium and magnesium compounds in untreated aluminum hydride are soluble in tetrahydrofuran and cannot be separated as insoluble products by dissolving the AlH_3 -1451.
- (x) There is an inverse relationship between the thermal stability and lithium content of Texas pilot plant aluminum hydride.
- (xi) The improvement in stability resulting from treatments at 60° and 80°C . (NBA and ethanol) compared to a 25°C . hydrolysis (pH 7) is due to conversion of lithium aluminum hydride (an impurity) to less reactive compounds by a combination hydrolysis and thermal decomposition.
- (xii) Decomposition occurs throughout the aluminum hydride crystal and is initiated at crystal discontinuities such as cracks, voids, and grain boundaries.
- (xiii) Stabilized samples must be dried to reduce "initial gassing." Drying by means of a warm stream of nitrogen may be the most practical method for large quantities.
- (xiv) The coating formed by the hydrolysis stabilization treatments is amorphous $\text{Al}(\text{OH})_3$. It cannot be identified by electron diffraction since it is amorphous, but helium densitometer results show a higher probability for $\text{Al}(\text{OH})_3$ than any other possible aluminum-oxygen compound.
- (xv) Stabilized magnesium-doped aluminum hydride is compatible with high energy plasticizers such as TVOPA.

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B. RECOMMENDATIONS (U)

(C) Based on an analysis of the results discussed in this report the following recommendations are made:

- (i) Treat most of the remaining Texas pilot plant aluminum hydride in n-butylamine containing 2% water for 5 days at 80°C. to improve its thermal stability.

Several pounds of pilot plant aluminum hydride should be reserved for further evaluation of stabilization techniques.

- (ii) Find methods to minimize the inclusion of lithium aluminum hydride in aluminum hydride, and, if possible, find less active desolvating agents to replace it.
- (iii) Find better ways to incorporate magnesium into the AlH_3 for improvements in thermal stability.
- (iv) Optimize the NBA-water stabilization technique. This would include treating for various periods of time and comparing the results with the present 5-day treatment. The effect of lesser amounts of water in the n-butylamine should also be determined.
- (v) Treat pound quantities of aluminum hydride by the ethanol-water stabilization technique for testing in propellant formulations. This should include propellant surveillance and the firing of 10-lb. motors made from this material to determine whether an oxygen content of approximately 2% in the aluminum hydride affects the specific impulse of the motor.
- (vi) Treat pound quantities of aluminum hydride by the combination 3-day pH 7 - 5-day treatment at 80°C. in diglyme containing (i) 2% water and (ii) 2% D_2O . Make the same test in propellants formulation as under (v).
- (vii) Develop a fluid bed dryer using heated nitrogen to dry large quantities of treated aluminum hydride.

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SECTION V

(U) GLOSSARY

(U)	AN	Acrylonitrile
(U)	DTA	Differential thermal analysis
(U)	TGA	Thermal gravimetric analysis
(U)	MTA	Mass thermal analysis
(U)	DPA	Diphenylacetylene
(U)	NBA	n-Butylamine
(U)	TEGDN	Triethylene glycol dinitrate
(C)	TVOPA	1,2,3-tris[1,2-bis(difluoroaminoethoxy) - propane]
(C)	PBEP	Poly[1,2-bis(difluoroamino)-2,3-epoxy- propane]

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SECTION VI

(U) REFERENCES

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2. (U) Private Communication, Dr. George Cann, Lockheed Propulsion Company, Redlands, California.
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APPENDIX A

(U) ELEMENTAL AND STABILITY DATA FOR TEXAS PILOT PLANT ALUMINUM HYDRIDE

(C) The following tables present the elemental analyses and stability data for Texas pilot plant samples, both "as received" and stabilized.

(U) Lot numbers are coded as follows: Reading from left to right, the first two digits refer to the month; the second two digits refer to the day and the last digit indicates the year. For example, Lot 08176 was manufactured on August 17, 1966.

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Table VII

(U) Elemental Analysis and Stability Data for AlH₃-1451, Lot 05316

Parameter	Treatment				
	"As Received" No Treatment	Hydrolyzed pH 7 15 min., 50 g.	Hydrolyzed pH 7 16 hr., 10 g.	Hydrolyzed pH 7 2 days, 10 g.	18 day NBA at 60°C., 50 g.
Composition, %					
Aluminum	87.50	87.40	87.35	87.0	86.3
Carbon	0.18	0.17	0.15	<0.10	0.1
Chlorine	0.26	0.09	0.10	0.07	0.07
Hydrogen	9.80	9.78	9.86	9.87	9.7
Lithium	0.25	0.18	0.21	0.19	0.17
Magnesium	1.05	1.07	1.07	1.14	1.04
Nitrogen	--	--	--	--	--
Oxygen	0.23	0.95	1.31	1.09	2.44
Stability, °C.					
Hrs. to 1%, 100°	4.1	8.7	8.9	9.3	12.5
Hrs. to 0.1%, 100°	0.75	1.8	--	--	--
Days to 1%, 60°	6.7	33	26	--	62
Days to 0.1%, 60°	3.0	7.5	5.5	--	--
					29
					6.0

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Table VIII
(U) Elemental Analysis and Stability Data for AlH₃-1451, Lot 11217

Parameter	As Received		Treatment		18 day NEA	
	No Treatment	Hydrolyzed 48 hr. pH 7, 15 g.	Hydrolyzed 10 d. pH 7, 5 g.	Hydrolyzed 17 d. pH 7, 5 g.	at 60°C. 22 g.	18 day NEA 592 g.
Composition, %						
Aluminum	87.7	87.2	85.2	82.7	86.5	86.4
Carbon	71	0.2	0.4	0.25	1.05	0.3
Chlorine	0.02	<0.05	<0.05	<0.05	<0.05	<0.05
Hydrogen	9.95	10.04	9.48	9.33	9.87	10.04
Lithium	0.16	0.17	0.15	0.13	0.17	0.17
Magnesium	1.56	1.69	1.62	1.66	1.60	1.60
Nitrogen	---	---	---	---	---	---
Oxygen	?	1.05	3.19	5.71	0.75	1.07
Stability						
Hr. to 1%, 100°	11.6	15.5	33.1	32.1	25.3	22.0
Hr. to 0.1%, 100°	3.0	---	6.0	---	---	3.7
Days to 1%, 60°	32	54	168	---	62	50
Days to 0.1%, 60°	7.5	14	---	---	17	14

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Table IX
(U) Elemental Analysis and Stability Data for AlH₃-1451, Lot 11177

Parameter	Treatment									
	"As Received" No Treatment	Hydrolyzed 48 hr. pH 7, 22 g.	Hydrolyzed 5 d. pH 7, 25 g.	Hydrolyzed 7 d. pH 7, 25 g.	Hydrolyzed 10 d. pH 7, 25 g.	Hydrolyzed 17 d. pH 7, 25 g.	18 day NBA 22 g. @ 60°C.	18 day NBA 22 g. @ 60°C.	18 day NBA 22 g. @ 60°C.	18 day NBA 22 g. @ 60°C.
Composition, %										
Aluminum	87.8	87.2	87.0	86.9	86.0	84.1	86.5	85.7		
Carbon	10.04	0.15	0.1	0.10	0.5	0.1	0.68	0.34		
Chlorine	0.15	<0.05	<0.05	<0.05	<0.05	<0.05	0.05	<0.1		
Hydrogen	10.04	9.84	9.87	9.83	9.45	8.99	9.85	9.84		
Lithium	0.15	0.14	0.14	0.15	0.14	0.14	0.17	0.15		
Magnesium	1.40	1.44	1.42	1.41	1.55	1.49	1.42	1.53		
Nitrogen	---	---	---	---	---	---	---	---		
Oxygen	---	0.87	1.13	1.48	2.89	5.06	0.78	1.11		
Stability										
Hr. to 1%, 100°	---	13.3	---	---	22	22.8	15.6	---		
Hr. to 0.1%, 100°	3.3	3.6	4.5	4.7	5.8	6.0	3.0	3.4		
Days to 1%, 60°	27	55	57	47	108	---	43	44		
Days to 0.1%, 60°	7	20	17	17	---	---	---	13		

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Table X

(U) Elemental Analysis - Thermal Stability Data
for AlH₃-1451, Lot 02028

Parameter	Treatment		
	"As Received" No Treatment	18-day NBA (2% H ₂ O) 60°C. 5-day pH 7	Combination 3-day pH 7, 5-day EtOH (2% H ₂ O) 80°C.
Composition, %			
Aluminum	87.1	87.7	87.9
Carbon	1.21	0.3	0.35
Chlorine	<0.05	<0.05	<0.05
Hydrogen	9.93	9.81	9.82
Lithium	0.17	0.17	0.16
Magnesium	1.3	1.2	1.2
Oxygen	0.43	1.0	1.55
Stability, °C.			
Days to 0.1%, 60°	3	14	33
Days to 1.0%, 60°	15	51	77

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Table XI

(C) Elemental Analyses and Thermal Stabilities of
Aluminum Hydride Without Magnesium (Blend I)

Parameter	Treatment			
	As Received	AN ^a	NBA ^b	Combina- tion ^c
Composition, %				
Aluminum	89.3	84.0	87.9	80.2
Carbon	0.3	0.6	0.2	0.6
Chlorine	<0.05	<0.05	<0.05	<0.05
Hydrogen	9.90	9.63	9.86	8.68
Lithium	0.18	0.17	0.18	0.16
Nitrogen	--	--	--	--
Oxygen	0.35	4.34	1.10	7.85
Stability				
Days to 0.1% Decomposition at 60°C.	2.5	4	3.5	6

^a17 days in acrylonitrile at 60°C.

^b5 days in n-butylamine at 80°C.

^c3 days at pH 7, then 5 days in ethanol at 80°C.

Table XII

(C) Elemental Analyses and Thermal Stabilities of
Magnesium-Doped Aluminum Hydride (Blend II)

Parameter	Treatment			
	As Received	AN ^a	NBA ^b	Combina- tion ^c
Composition, %				
Aluminum	88.1	85.1	87.0	85.9
Carbon	0.1	0.4	0.15	0.1
Chlorine	<0.05	0.0	0.05	<0.05
Hydrogen	9.89	9.72	9.95	9.77
Lithium	0.16	0.16	0.16	0.14
Nitrogen	--	--	--	--
Oxygen	0.27	2.53	0.96	2.17
Stability				
Days to 0.1% Decomposition at 60°C.	3.5	14	17	23

^a17 days in acrylonitrile at 60°C.

^b5 days in n-butylamine at 80°C.

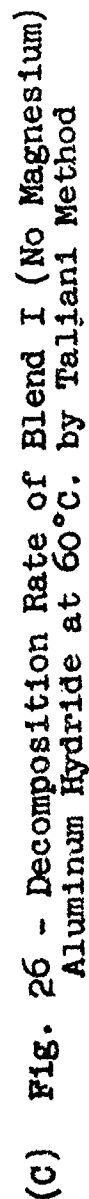
^c3 days at pH 7.

CONFIDENTIALAPPENDIX BTHERMAL STABILITY CURVES OF AlH_3 -1451 PREPARED FOR
PROPELLANT EVALUATION BY
LOCKHEED PROPULSION COMPANY

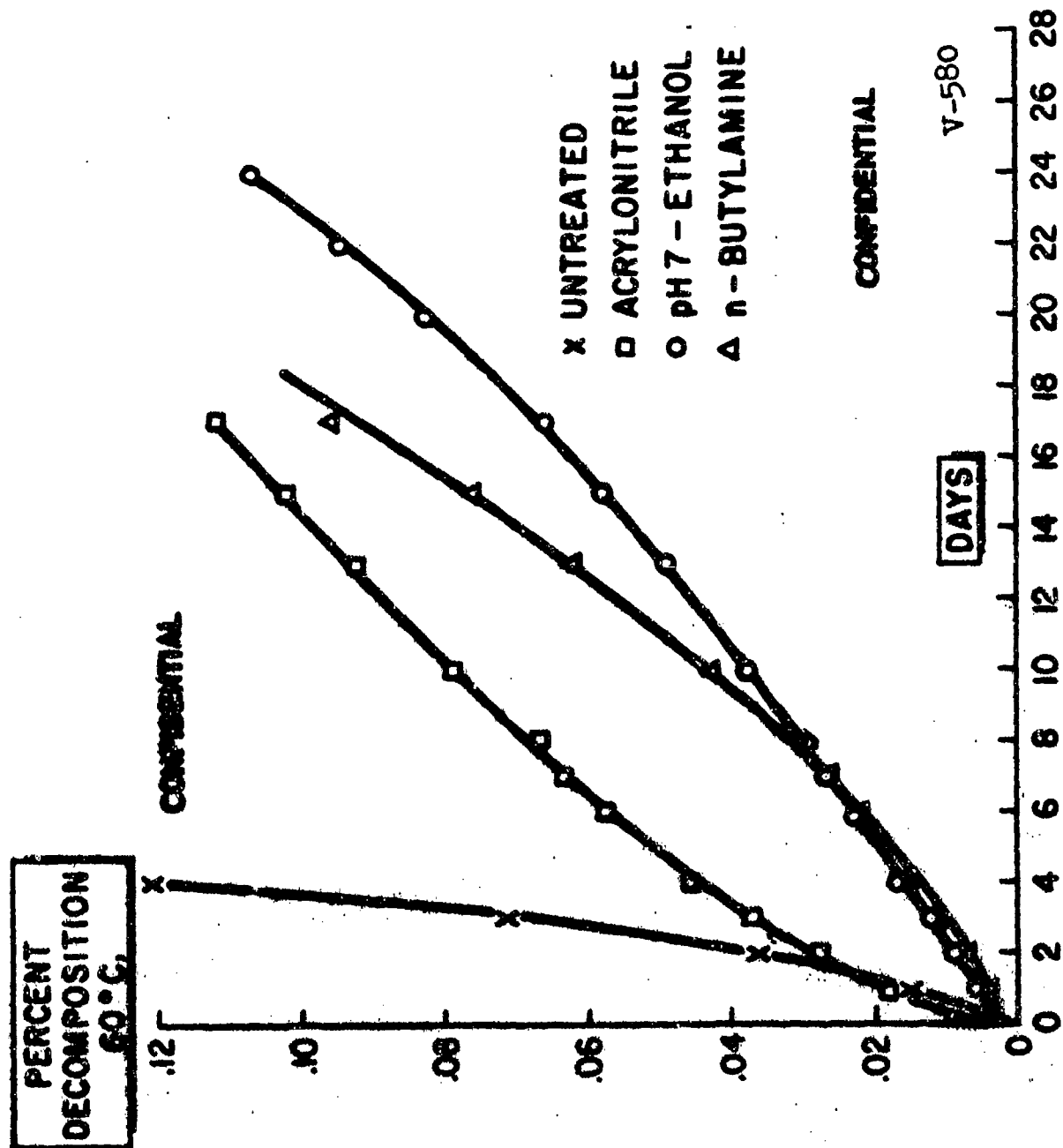
(C) The following graphs (Figures 26-33) illustrate the thermal stability of both non-doped and magnesium-doped aluminum hydride. Blend I was a composite of 9 lots of non-doped AlH_3 -1451 totaling 13.7 pounds. Blend II was a composite of 10 lots of magnesium-doped DPA-treated AlH_3 -1451 totaling 16.2 pounds. Each lot of Blend II originally required between 18 1/2 and 22 days to reach 1% decomposition. Prior to stabilization treatments the DPA was removed by an ether wash. This reduced the time for Blend II to reach 1% decomposition at 60°C. to 11 days.

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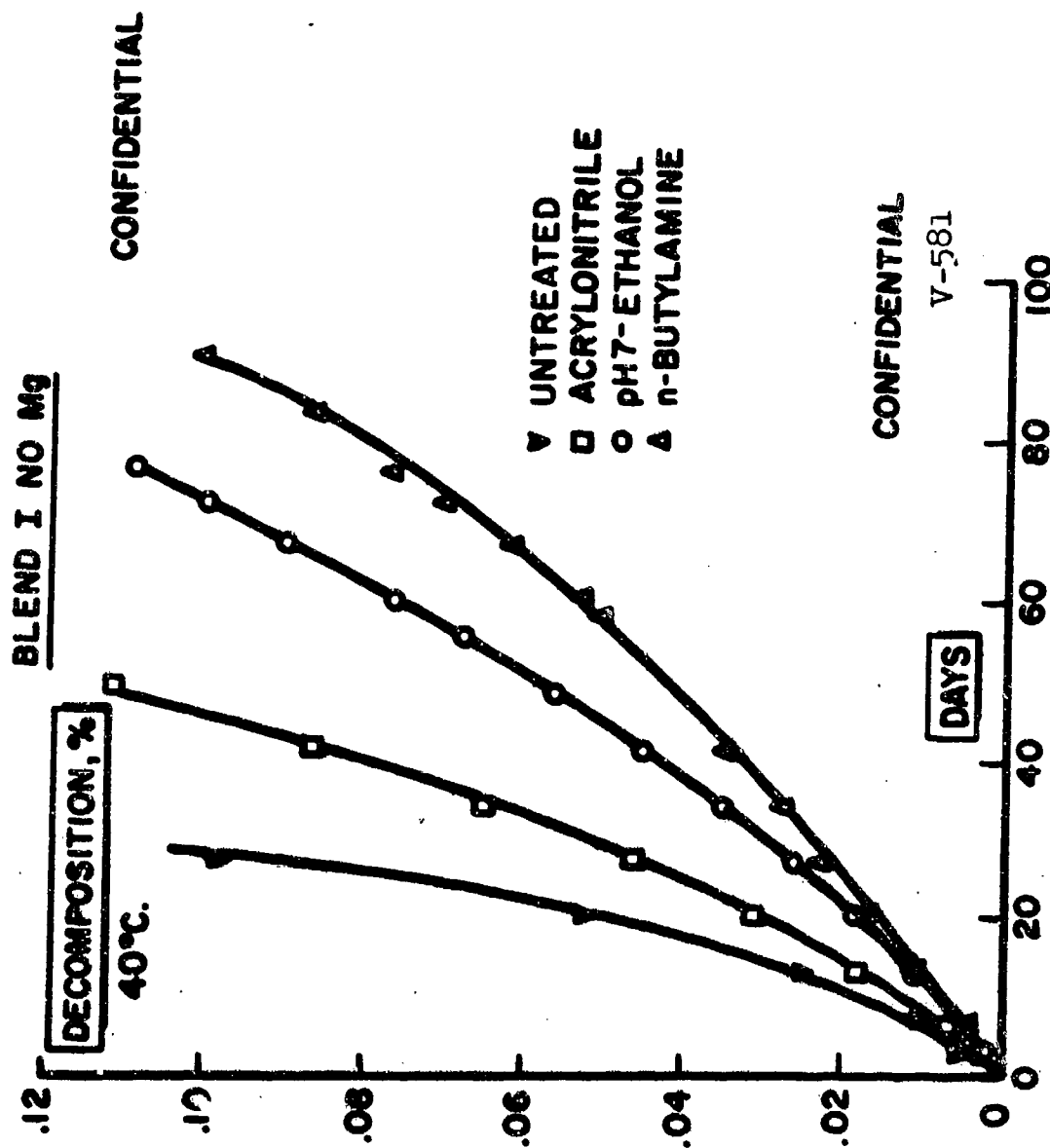


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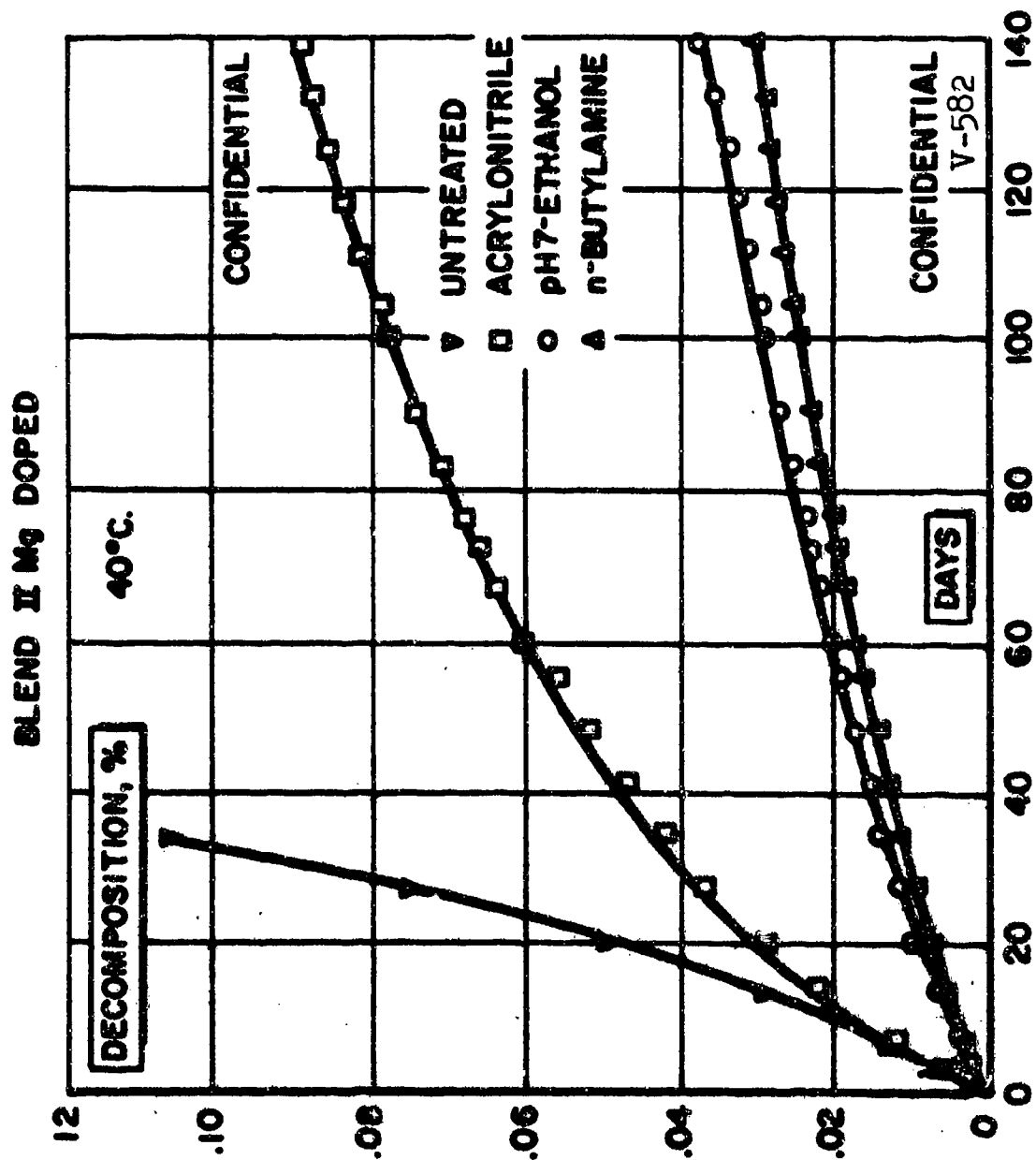
CONFIDENTIAL**BLEND II Mg DOPED**

(c) Fig. 27 - Decomposition Rate of Blend II (Magnesium-Doped) Aluminum Hydride at 60°C. by Taliani Method

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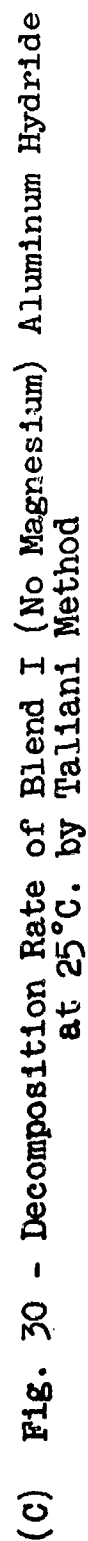


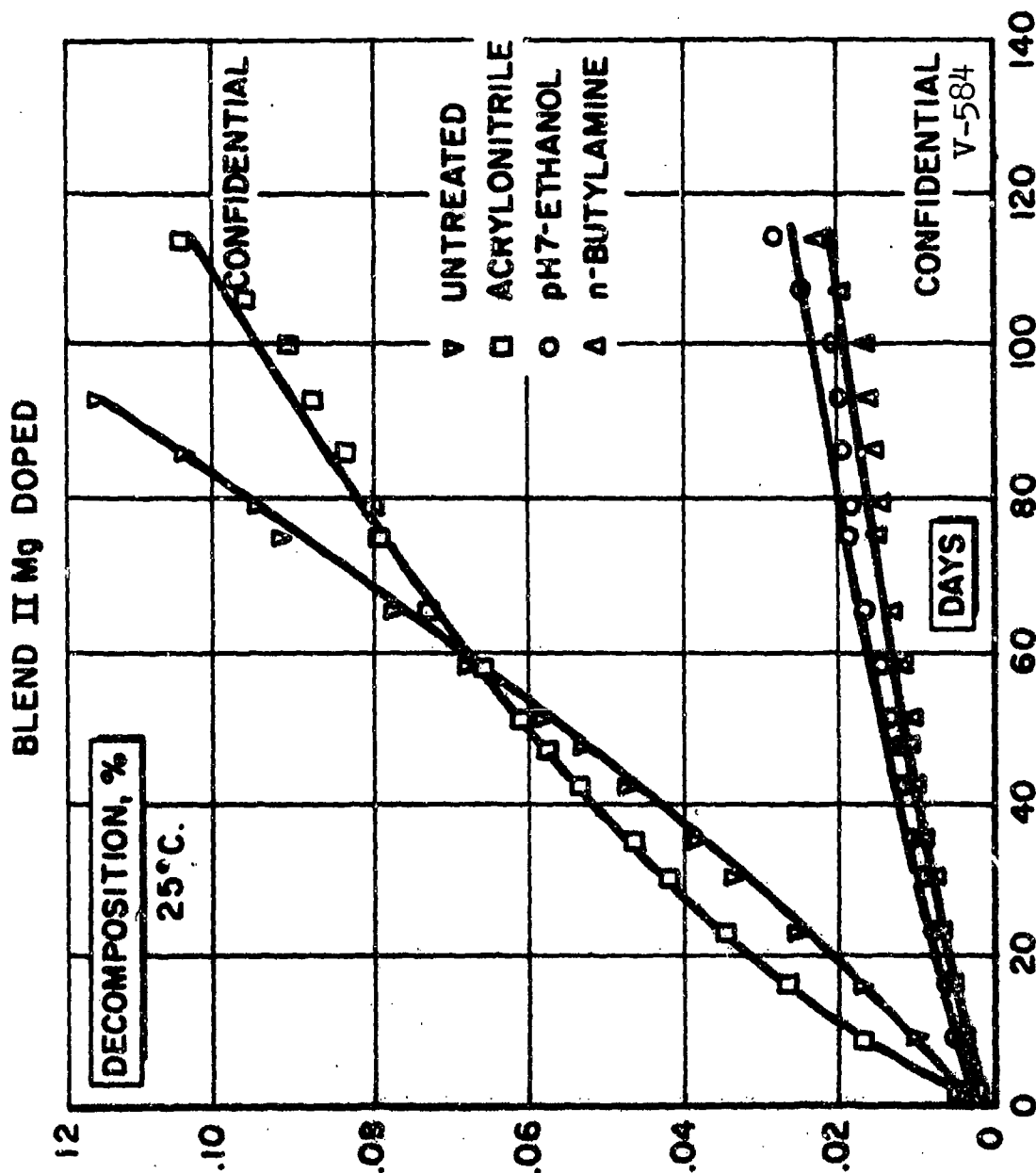
(C) Fig. 28 - Decomposition Rate of Blend I (No Magnesium) Aluminum Hydride at 40°C. by Taliani Method

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(C) Fig. 29 - Decomposition Rate of Blend II (Magnesium Doped) Aluminum Hydride at 40°C. by Taliani Method

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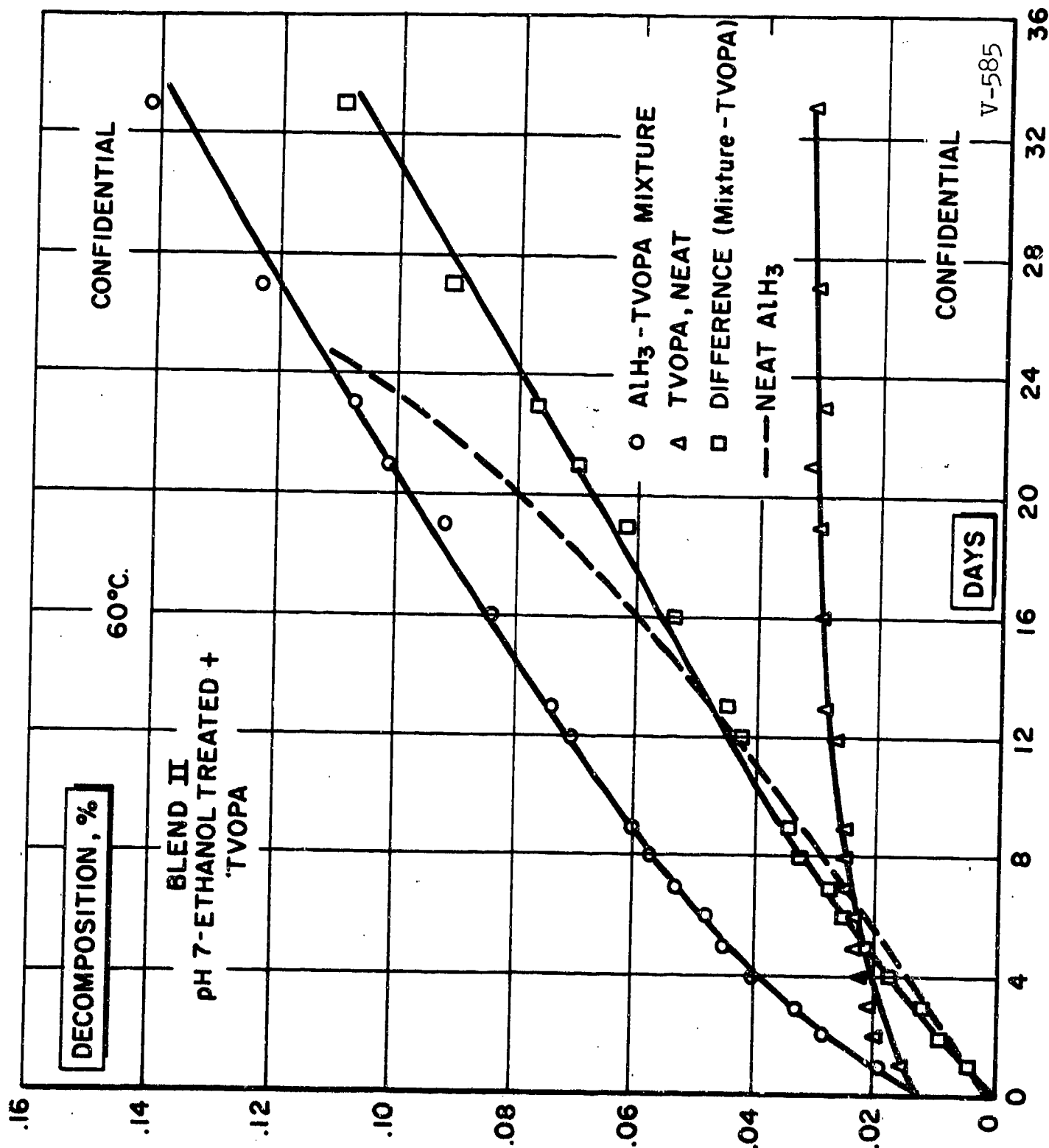
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(C) Fig. 31 - Decomposition Rate of Blend II (Magnesium Doped) Aluminum Hydride at 25°C. by Taliani Method

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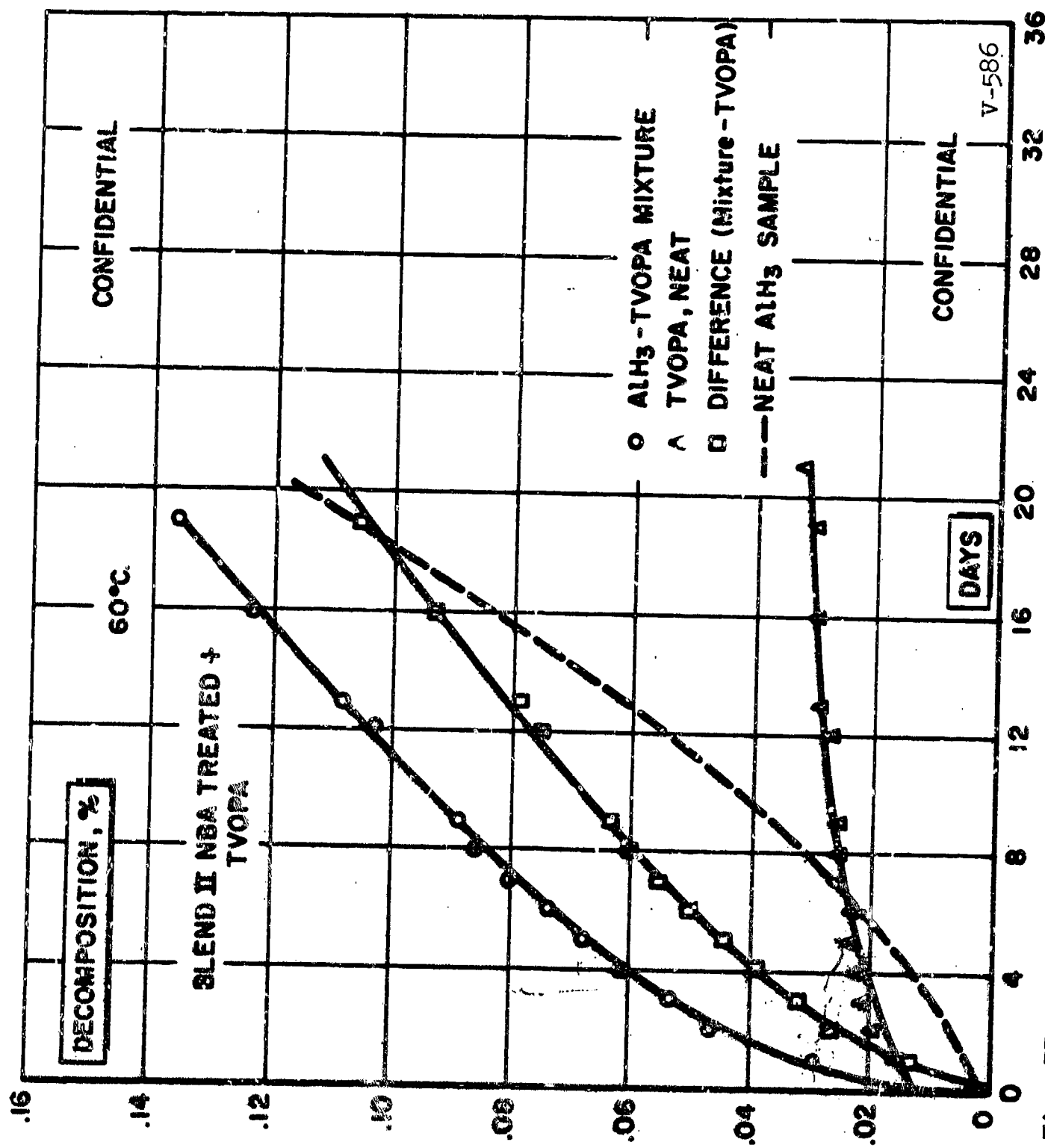
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(C) Fig. 32 - Compatibility of Blend II (Magnesium Doped pH 7 - Ethanol Treated Aluminum Hydride With TVOPA at 60°C. by Taliani Method

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(C) Fig. 33 - Compatibility of Blend II (Magnesium Doped) NBA Treated Aluminum Hydride With TVOPA at 60°C. by Taliani Method

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APPENDIX C

(U) n-BUTYLAMINE TREATMENT OF AlH₃-1451

(C) In a typical treatment of AlH₃-1451 with n-butylamine (2% H₂O) the following procedure has been most successfully used. One part AlH₃-1451 is slurried in five parts reagent grade n-butylamine containing 2% water after which slurry is heated at 80°C. under nitrogen for 5-days. Maintaining the bath temperature at 80°C. provides a gentle reflux of the n-butylamine (b.p. 77.8°C.). The motion due to the boiling provides sufficient stirring of the sample during treatment. The hydride is recovered either by decanting the treatment liquor or by filtration. The product is dried under vacuum at 60°C. for two hours (NOTE: n-Butylamine has a high vapor pressure and is quite flammable).

(C) The drying procedure removes adsorbed water and minimizes subsequent reaction of the water with the AlH₃-1451, thus eliminating any further gassing. Although the drying was successfully carried out at ambient temperature, it was also shown that the heat treatment at 60°C. is beneficial in removing the last traces of water.

CONFIDENTIALAPPENDIX D(C) PROCEDURE FOR STABILIZING AlH₃-1451
BY CONTROLLED HYDROLYSIS (pH 7)

(U) For each gram of material, 10 ml. of the pH 7 buffer (prepared by dissolving 6.15 g. of KH₂PO₄ in 500 ml. of water, adding 267 ml. of 0.1 N NaOH, and making up to 1 liter with distilled water) is used. The preferred method is to add the hydride to the buffer solution with stirring. The reaction between active hydride sites and water under these conditions is not violent, and there is sufficient buffer to maintain the pH of the solution at 7.0. A lower ratio of solution to hydride can result in the solution becoming basic, with a corresponding increase in reaction rate. Quantities up to one pound of hydride have been treated without noticeable evolution of heat, but, before treating large amounts, it is advisable to make a pilot run with a few grams of hydride to determine the possible presence of exceptionally reactive materials.

(C) The hydrolysis time can vary from a few minutes to several days. Material which has not been DPA-treated and consequently is not water-repellent usually requires from 15 to 45 minutes to realize a significant improvement in stability and maintain a low oxygen content. DPA-treated hydride with good heat stability requires 2-3 days in the buffer solution to realize a two- to threefold improvement in thermal stability and maintain an oxygen content of about 1%.

(U) Much of the DPA from the samples will float on the surface of the buffer or adhere to the walls of the containers. After hydrolysis, it no longer appears to affect the thermal stability, so its removal is not detrimental to the sample.

(U) After the pH 7 treatment, the buffer solution is decanted from the hydride and the hydride washed three times with water. Each wash is decanted from the solid as soon as possible, and following the last wash, the product is either dried directly or washed with acetone. The latter method has the advantage of removing excess water, thus speeding up the drying process and simultaneously removing excess DPA. No significant difference between product dried by the two methods was observed.

(U) The hydride should be vacuum dried overnight at room temperature, followed by heating at 60°C. under vacuum (<5 μ) for two hours. This step removes the last traces of water and prevents "initial gassing," which is always observed for hydrolyzed samples dried at ambient temperature only.

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13. ABSTRACT		
<p>(C) The thermal stability of magnesium-doped aluminum hydride can be increased seven- to tenfold by controlled hydrolysis treatments; compatibility with propellant ingredients is also greatly improved. A 5-day n-butylamine (2% H₂O) treatment at 80°C. is recommended for future use. Scanning electron photomicrographs reveal the surface characteristics of aluminum hydride crystals and show a thin coating, probably Al(OH)₃, generated by hydrolysis treatments. Metallographic studies show that decomposition occurs throughout the crystal, particularly at discontinuities such as voids, cracks, and grain boundaries. Ion probe mass spectroscopy shows a higher lithium content near the surface than in the interior of the crystals. Lithium aluminum hydride was extracted from AlH₃-1451 and is believed to be responsible for nucleation sites which result in the decomposition of AlH₃. Pound quantities of stabilized AlH₃ have been successfully used in high energy propellant formulations.</p>		

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KEY WORDS	LINE A		LINE B		LINE C	
	ROLE	WT	ROLE	WT	ROLE	WT
Aluminum Hydride						
Hydrolysis						
Stability						
Compatibility						

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